

Time-Dependent Density Functional Theory for Nonadiabatic Processes

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Abstract. Time-dependent density functional theory (TDDFT) is a general and robust method allowing the study of electron dynamics whether induced by nuclear motion or by external fields. We give a brief overview of the theory and some numerical methods together with recent applications stressing the generality and wide applicability of the method. We also discuss recent attempts to extend the present TDDFT by incorporating memory terms into the exchange correlation potentials.

1. INTRODUCTION

Time-dependent density functional theory¹ (TDDFT) is emerging as a general and reliable tool for studying processes involving electron dynamics in molecular systems, metal surfaces, and nano-structures. In this brief review, we outline the theory of TDDFT and present selected recent applications, with emphasis on the generality of the method. We also discuss some recent advances in incorporating memory effects into TDDFT.

A. Basic TDDFT

Molecular processes are conveniently described by a Born–Oppenheimer picture, where the nuclei coordinates, collectively denoted by $\mathbf{R} = (R_\mu)$, serve as parameters in an electronic Hamiltonian

$$\hat{H}_e[\mathbf{R}](t) = \hat{T} + \hat{V}[\mathbf{R}](t) + \hat{U} \quad (1.1)$$

where

$$\hat{T} = \frac{-1}{2} \sum_{q=1}^{N_e} \nabla_q^2 \quad (1.2)$$

is the kinetic energy operator, N_e the number of electrons, and atomic units $\hbar = m_e = a_0 = 4\pi\epsilon_0 = 1$ are assumed throughout. In the Hamiltonian of eq 1.1 there are two types of potential energy terms. The one-electron potential energy is

$$\hat{V}[\mathbf{R}](t) = \sum_{q=1}^{N_e} v[\mathbf{R}](\mathbf{r}_q, t) \quad (1.3)$$

Here $v[\mathbf{R}](\mathbf{r}_q, t)$ is the time-dependent external potential operating on each electron. This potential depends on the nuclear position and possibly on time (if either external fields are present or the nuclei themselves are moving). The potential energy of Coulombic repulsion between pairs of electrons is given by

$$\hat{U} = \frac{1}{2} \sum_{q \neq q'=1}^{N_e} \frac{1}{r_{qq'}} \quad (1.4)$$

All aspects of the electron dynamics can be determined from the time-dependent wave function $\psi(t)$ evolving from the known initial state. We henceforth assume the nuclei initial position is \mathbf{R}_0 at $t = 0$ and the electronic wave function at that position is the ground-state of $\hat{H}_e[\mathbf{R}]$ ($t = 0$). The TD wave function $\psi(t) \equiv \psi(x_1 \dots x_{N_e}, t)$ (where x_q are the spatial and spin coordinates of electron q) can be determined by solving the time-dependent Schrödinger equation

$$i\dot{\psi}(t) = \hat{H}_e[\mathbf{R}](t)\psi(t) \quad (1.5)$$

This however is a formidable task because of the electron–electron interaction, and thus it is impossible for any but single-electron molecules.

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If electrons were non-interacting, then solving eq 1.5 is “easy”. By that we mean that the numerical effort is linear with the number of electrons. We explain this here in some detail now.

When $\hat{U} = 0$ in eq 1.1 the ground-state $\psi(t=0)$ can be taken as a single Slater determinant, D , composed of N_e single-electron spin-orbitals $\phi_q(x)$

$$D[\phi_1 \dots \phi_{N_e}] = \frac{1}{\sqrt{N_e!}} \det[\phi_1(x_1) \dots \phi_{N_e}(x_{N_e})] \quad (1.6)$$

Furthermore, under a time-dependent field, the evolving wave function remains a single determinant; each of the spin-orbitals evolves from its initial state by the *same* single-electron Hamiltonian

$$\hat{H}_1 = \frac{-1}{2} \nabla^2 + v[\mathbf{R}](\mathbf{r}, t)$$

Thus determining the dynamics of N_e electrons can be done by solving N_e 3-D Schrödinger equations. Let us denote by Z_1 the time or memory needed for solving a 1-D Schrödinger equation. Obviously, the time to solve an N-D equation is about $\propto Z_1^N$. So, in our case, since we are solving N_e 3-D equations, the time goes as $\propto N_e Z_1^3$. The important observation here is that this is *linear in the number of electrons*. On the other hand, when electron interaction is present ($\hat{U} \neq 0$ in eq 1.1), one deals with a *single* Schrödinger equation of $3N_e$ dimensions. The time or memory involved is now $Z_1^{3N_e}$, that is, the number of electrons *appears in the exponent* and the problem is therefore “hard” or, more precisely, it becomes totally intractable as the number of electrons grows!

TDDFT tries to bypass the exponential scaling by avoiding the electronic wave function and concentrating instead on a simpler quantity, the 1-electron density

$$n(\mathbf{r}, t) = \langle \psi(t) | \hat{n}(\mathbf{r}) | \psi(t) \rangle \quad (1.7)$$

i.e., the instantaneous expectation value of the electron density operator, the number of electrons per unit volume at any given point \mathbf{r} in 3-D physical space

$$\hat{n}(\mathbf{r}) = \sum_{q=1}^{N_e} \delta(\mathbf{r} - \mathbf{r}_q) \quad (1.8)$$

By using eq 1.8 in 1.7, $n(\mathbf{r}, t)$ is the integral of $|\psi(x_1, x_2, \dots, x_{N_e}, t)|^2$ over the coordinates of electrons 2 to N_e and the spin coordinates of electron 1.

If useful equations of motion for $n(\mathbf{r}, t)$ could be found, then their solution would be easy because $n(\mathbf{r}, t)$ is a 3-D object. In order to devise such equations, we set up a mapping between the “hard” interacting electron system and an “easy” fictitious system of non-interacting electrons that has the same time-dependent density

$n(\mathbf{r}, t)$. This is analogous to what is done in the ground-state density functional theory.² Since it is easy to determine the dynamics of non-interacting electrons, this can be a viable way to proceed.

Of course, the external potential on the non-interacting system, denoted $v_s(\mathbf{r}, t)$, must be different from that of the interacting system— $v(\mathbf{r}, t)$. It must be built in such a way that the non-interacting electron density $n(\mathbf{r}, t)$ retraces exactly that of the interacting system. If we knew $v_s(\mathbf{r}, t)$ and the initial Slater-determinant of the non-interacting system then we could solve the N_e 3-D Schrödinger equations, called the TD Kohn–Sham equations:

$$i\dot{\phi}_q(\mathbf{r}, t) = -\frac{1}{2} \nabla^2 \phi_q(\mathbf{r}, t) + v_s(\mathbf{r}, t) \phi_q(\mathbf{r}, t) \quad (1.9)$$

and get the density from

$$\begin{aligned} n(\mathbf{r}, t) &= \langle D[\phi_1 \dots \phi_{N_e}](t) | \hat{n}(\mathbf{r}) | D[\phi_1 \dots \phi_{N_e}](t) \rangle \\ &= \sum_{q=1}^{N_e} |\phi_q(\mathbf{r}, t)|^2 \end{aligned} \quad (1.10)$$

Does such a potential $v_s(\mathbf{r}, t)$ exist? And if it does, is it unique? The answer to the first question is: not always. The answer to the second is: yes; Runge and Gross¹ gave a reasonably general proof for this. They proved that for a given initial state of any system whether interacting or not, all potentials that give the same density $n(\mathbf{r}, t)$ are different by at most an additive purely time-dependent constant.

The following picture emerges. Given an interacting system starting from a given initial state $\psi(t=0)$, we try to find a non-interacting system, starting from a compatible determinant (having the density $n(\mathbf{r}, t=0)$) that experiences a potential $v_s(\mathbf{r}, t)$ constructed such that both systems have the same density.

How can we determine this unique potential (which does not always exist)? There is no general answer to this question. What we do in practice is use an approximation which feeds on the successful approximate approaches of density functional theory. We write the unknown potential as a sum of three terms

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{XC}(\mathbf{r}, t) \quad (1.11)$$

The first two terms on the right are the external potential (the same as the potential on the interacting system) and the instantaneous Coulomb repulsion potential, called the “Hartree” potential

$$v_H(\mathbf{r}, t) = \int \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad (1.12)$$

The third term, called the exchange-correlation

potential (XC) is in principle unknown. It is assumed that $v_{XC}(\mathbf{r}, t)$, which depends on the history of the density $n(\mathbf{r}', t')$ for $t' \leq t$, is reasonably easy to approximate. The most common approximation is a temporarily local approximation, valid when the temporal variations in the density are small, but widely used beyond this assumption. It obviously neglects memory effects. In this approximation, the XC potential functional takes the general form

$$v_{XC}[n](\mathbf{r}, t) = F(n(\mathbf{r}, t), |\nabla n(\mathbf{r}, t)|, \nabla^2 n(\mathbf{r}, t), \dots) \quad (1.13)$$

where F is an appropriate function, derived from the theory of a simplified system, for example the homogeneous electron gas. In order to have consistency with the DFT analog, F is chosen equal to the analogous ground-state function. The adiabatic local density approximation is the simplest example of such an approach. In the local density approximation,² the XC potential for the ground state is taken to be

$$v_{XC}(\mathbf{r}) = \varepsilon_{XC}(n_0(\mathbf{r})) + n_0(\mathbf{r}) \varepsilon'_{XC}(n_0(\mathbf{r})) \quad (\text{ground state}) \quad (1.14)$$

where $\varepsilon_{XC}(n_0)$ is the exchange correlation energy per particle of the homogeneous electron gas in its ground state at density n_0 . This potential is exact for the homogeneous electron gas. Using it for non-homogeneous systems is an approximation. This approximation works surprisingly well for molecules, even though they are far from being homogeneous systems. The adiabatic local density approximation, ALDA, assumes that the form (eq 1.14) is valid for the time-dependent case. This amounts to assuming $F(n, \dots) = \varepsilon_{LDA}(n) + n \varepsilon'_{LDA}(n)$, in eq 1.13.

Despite the crude approximations of ALDA, it was found to be quite robust and at times as accurate as more involved and rigorous wave function methods^{3,4}. In Section 4, we will describe some recent progress in developing functionals that go beyond the ALDA by incorporating memory effects.

The assumption of spatial locality for v_{XC} in eq 1.13 leads to problems of self-interaction, inherited from local DFT functional. Self-interaction is a real detriment in a large class of DFT applications: anions are often erroneously predicted unbound, charge transfer is incorrectly described, ionization energy is not well described by orbital energies, polarizability is grossly exaggerated for elongated molecules. Methods that correct for these problems have been suggested and their utility is the subject of recent investigations.⁵⁻⁹ We should at this point mention a popular method, that has been developed long before TDDFT, the time-dependent Hartree–Fock (TDHF) method and its linear-response develop-

ment called random-phase approximation (RPA) (we refer the reader to ref 10 for a detailed review on TDHF and RPA). This theory does not suffer from self-interaction, but for electron dynamics in molecules is not sufficiently accurate as it does not explicitly treat electron correlation and therefore often leads to larger errors than TDDFT in excitation energies of molecules.¹¹

B. Ehrenfest Molecular Dynamics

Up to now, we have not discussed the nuclei beyond assuming that their coordinates are parameters in the electronic dynamics. In general, the nuclei must be treated as quantum particles. However, because of their large mass, for some processes they can be considered as classical. Classical nuclei obey Newton's equations of motion

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = \mathbf{F}_I^e + \sum_j \frac{Z_j Z_I}{|\mathbf{R}_I - \mathbf{R}_j|} \quad (1.15)$$

where I indexes the different nuclei (of mass M_I and charge Z_I) and \mathbf{F}_I^e is electronic force on the I th nucleus.

We mention two cases where it is common to assume that classical nuclei can give a reasonable approximation to dynamical processes. First, is the Born–Oppenheimer (BO) approximation.¹² The basic application of this approximation assumes slow nuclei and highly spaced electronic levels. The approximation however breaks down when electronic levels approach each other. The ultimate breakdown of the BO approximation is in a real crossing of levels, known as conical intersections.^{13,14} When BO approximation is valid, only DFT needs to be employed since electrons are assumed to be in the ground state. One can use DFT to obtain the ground-state adiabatic potential and use this potential for a quantum treatment of the nuclear dynamics.^{15,16} In this case, the electronic force \mathbf{F}_I^e on nucleus I is given by

$$\mathbf{F}_I^e = \int n_0[\mathbf{R}](\mathbf{r}) \nabla_{\mathbf{R}_I} v[\mathbf{R}](\mathbf{r}) d^3r \quad (1.16)$$

where $n_0[\mathbf{R}](\mathbf{r})$ is the ground-state electron density at \mathbf{r} when the nuclei configuration is \mathbf{R} .

Another case where the classical approximation for nuclei can be justified is when a large number of electronic excitations exist and nuclear dynamics is governed by an *average* electronic force. This is the basis for the mean-field or commonly called Ehrenfest molecular dynamics.¹⁷ The force \mathbf{F}_I^e on nucleus I in this approach is thus given by the Hellman–Feynman force

$$\mathbf{F}_I^e = \int n(\mathbf{r}, t) \nabla_{\mathbf{R}_I} v[\mathbf{R}(t)](\mathbf{r}) d^3r \quad (1.17)$$

This approach is appropriate when the dynamics on

all excited-state surfaces is similar. It is often assumed that such is the case, for example, when nuclei move in or near metals: the electron–hole pair excitations are expected to give nearly parallel surfaces. We study such a case in Section 2C below. Another system where this type of approximation may be appropriate is a molecule interacting with a super-strong electric field. In this case, the amount of energy absorbed by the molecule is huge and the classical dynamics approximation is expected to be valid.

C. TDDFT in Real Time—Numerical Methods

In this review we concentrate on applications which make use of the real-time Kohn–Sham equations (eq 1.9). This approach is different from the more popular applications of TDDFT, done in the frequency domain (which are limited to linear or low-order response theory).^{18–20} Several groups are developing real-time TDDFT applications and should be consulted.^{21–24}

In order to apply the TDDFT theory we need a numerical method to represent the Kohn–Sham orbitals, the various electronic operators, such as kinetic energy, Hartree potential, and other types of potential. To these we add a method that effectively propagates the orbitals in time.

The applications below all use the plane-waves basis for representing the molecular orbitals. This method is well described in plane-waves DFT reviews.^{15,16} The essential idea is that the system is placed in a rectangular Cartesian cell, spanning $|x| < L_x$, $|y| < L_y$, and $|z| < L_z$. A uniformly spaced grid of N_x , N_y , and N_z points is introduced, with grid spacing $\Delta x = 2L_x/N_x$ (and similar definitions for y and z directions). Typically, $\Delta x = \Delta y = \Delta z$. Using Fourier methods, the kinetic energy operator and the Coulomb potential (eq 1.12) can be efficiently calculated. One crucial element is the use of pseudopotentials,^{25–27} which is needed since core electrons and potentials are not well presented on equally spaced grids.

There is a variety of methods to enforced time evolution. We have used a Chebyshev collocation method in the past.^{28,29} This method achieves very high accuracy, but when such high accuracy is not needed, it is rather expensive. The applications below are usually done using a 5th-order Runge–Kutta adaptive method.³¹ To explain this approach we rewrite the Kohn–Sham equations (eq 1.9) as

$$i\dot{\phi}_q(\mathbf{r}, t) = \hat{H}_{KS}[n(\mathbf{r}, t)]\phi_q(\mathbf{r}, t) \quad (1.18)$$

Where $\hat{H}_{KS}[n] = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}, t)$ is the Kohn–Sham Hamiltonian, depending on the instantaneous electron density. These are nonlinear, explicitly time-dependent equations. We move to the kinetic-energy interaction representation, defining

$$\varphi_q(\mathbf{r}, t) = e^{i\hat{T}t}\phi_q(\mathbf{r}, t) \quad (1.19)$$

where \hat{T} is the one-electron kinetic energy operator. The equation of motion of φ_q is

$$i\dot{\varphi}_q(\mathbf{r}, t) = \hat{H}_I[n](t)\varphi_q(\mathbf{r}, t) \quad (1.20)$$

where

$$\hat{H}_I[n](t) = e^{i\hat{T}t}v_s[n](\mathbf{r}, t)e^{-i\hat{T}t} \quad (1.21)$$

and $n(\mathbf{r}, t)$ is given by eq 1.10. The eigenvalue range of v_s is often considerably smaller than that of \hat{H}_{KS} . This is because of the absolute dominance of kinetic energy for the high energy spectrum of \hat{H}_{KS} , a typical property of Coulomb interactions. The application of the operator $e^{\pm i\hat{T}t}$ on a wave function is efficiently and accurately performed using fast-Fourier methods.³⁰

The solution of eq 1.20 is done using a standard 5th order Runge–Kutta method with adaptive step size.³¹ This kinetic-energy dressing of the Hamiltonian allows a larger step size to be taken in the Runge–Kutta propagation. When the kinetic energy is not dominant, one can either use the same Runge–Kutta method directly on eq 1.18 or use another separable Hamiltonian $\hat{H}_{sep} = \hat{H}_x + \hat{H}_y + \hat{H}_z$ instead of \hat{T} .

D. Absorbing Potentials

Another essential element in some of the calculations is the absorption of electron flux that approaches the grid boundaries. This is done by introducing a complex potential^{32,33} of the form

$$w(x) = \alpha(1-i)(L_x - |x|)^3 \theta(|x| - (L_x - l_x)) \quad (1.22)$$

where l_x is the width of the potential, α a real number, and $\theta(\xi)$ is the Heaviside function, 1 for $\xi > 0$ and 0 for $\xi < 0$. Similar expressions are used for the absorbing potential in the y and z directions. These two parameters can be estimated by requiring a given threshold for reflection/transmission, as described in ref 34.

2. APPLICATIONS

All applications below use a plane-waves basis and Troullier–Martins norm-conserving pseudopotentials for the H-atoms,^{25,26} within the Kleinman–Bylander²⁷ ansatz. In these calculations we also used the local spin-density functional of Perdew and Wang.³⁵

A. Photoabsorption Cross Sections

The photoabsorption cross sections is the imaginary part of the dipole–dipole correlation function³⁶

$$\sigma_{ph}(\omega) = \omega e^2 / 2c\hbar\epsilon_0 \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [\hat{z}(t), \hat{z}]_0 \rangle \quad (2.1)$$

where $\hat{z}(t)$ is the electron dipole operator.

We use linear response theory to calculate this quantity. When we very gently perturb a system initially in

its ground state by a time-dependent pulse, the response of the system is linear with pulse strength. We use a field that couples to the system through some observable of the form

$$\hat{\pi} = \sum_{q=1}^{N_e} \pi(\mathbf{r}_q)$$

where N_e is the number of electrons and \mathbf{r}_q is the position of the q th electron. The Hamiltonian controlling the time-dependent evolution of the electrons is

$$\hat{H}(t) = \hat{H}_e + \eta f(t) \hat{\pi} \quad (2.2)$$

Here η is the field strength and $f(t)$ is a pulse of duration $\approx T$

$$f(t) = e^{-\frac{(t-T_0)^2}{2T^2}} \quad (2.3)$$

For application to eq 2.1 we will choose the perturbing operator $\hat{\pi}$ to be the z -component of the dipole operator: $\pi(\mathbf{r}) = ez$. Other observables may be used for other types of calculations, as we discuss in the next section. The perturbation drives the system into motion resulting in a time-dependent wave function $\psi(t)$. Soon, the external field dies out (because $f(t)$ decays rapidly), but the motion it stirred up remains. The expectation value $\langle \hat{Y}(t) \rangle = \langle \psi(t) | \hat{Y} | \psi(t) \rangle$ of some operator

$$\hat{Y} = \sum_{q=1}^{N_e} y(\mathbf{r}_q)$$

can be written using linear response theory as a correlation function³⁷

$$\Delta Y(t) = \langle \hat{Y}(t) \rangle - \langle \hat{Y}(0) \rangle = \eta \int_0^\infty f(t-\tau) C(\tau) d\tau \quad (2.4)$$

where $C(\tau) = i \langle [\hat{\pi}, \hat{Y}(\tau)] \rangle$ is the correlation function. The signal $\Delta Y(t)$ is also given by the expression

$$\Delta Y(t) = \int [n(\mathbf{r}, t) - n_{gs}(\mathbf{r})] y(\mathbf{r}) d^3r \quad (2.5)$$

where $n(\mathbf{r}, t=0) = n_0(\mathbf{r})$ is the ground-state density. So $\Delta Y(t)$ can be calculated directly using TDDFT, then the correlation function of eq 2.4 can be computed from it. This can be done using Fourier methods since, taking the Fourier transform of eq 2.4 and solving for the correlation function, one obtains

$$\tilde{C}(\omega) = \frac{\Delta \tilde{Y}(\omega)}{\eta \tilde{f}(\omega)}$$

where the tilda'd quantities are the Fourier transforms of their time domain quantities.

Taking $\hat{\pi} = \hat{Y} = \hat{z}$ in this theory gives a practical way to determine the photoabsorption spectrum of eq 2.1.

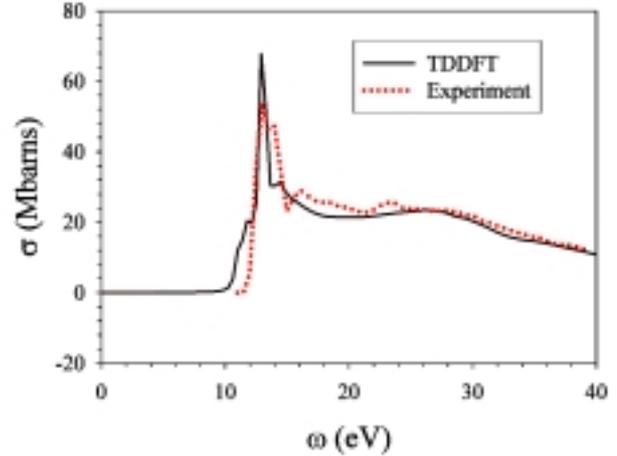


Fig. 1. The photoabsorption spectrum of N_2 —experiment³⁸ (dotted) vs. TDDFT calculation (line) within the adiabatic local density approximation. There are no fitting parameters used here.

We demonstrate the applicability of the theory to the N_2 molecule, assuming nuclei are clamped with N_2 bond length of $R_e = 1.1 \text{ \AA}$. We compare the calculated cross sections with experiment³⁸ in Fig. 1. For this calculation we used a cubic box of edge of $36 a_0$ (i.e., $L_x = L_y = L_z = 18 a_0$). Such a large box is needed because of the large width l of the complex absorbing potential (eq 1.22), taken as $11 a_0$. The second parameter of the absorbing potential is $\alpha = 3.8 \times 10^{-4} E_h$. These parameters ensure 99% absorption by the complex potential for electronic waves in the energy range 1 eV – 40 eV. We have carefully checked for reasonable convergence of all results with respect to all parameters. Thus, this is a calculation from first principles in the sense that we have not attempted to fit the results to experiment. From Fig. 1 it can be seen that the ALDA-based calculation cannot account for all experimental features. Still, the correspondence is quite impressive considering the huge photon energy range covered. Calculations on additional molecules show similar behavior and will be discussed in a future paper.³⁹

B. Nonadiabatic Couplings

In the Born–Oppenheimer (BO) picture the electrons in a molecule affect the nuclear dynamics via two types of quantities: *adiabatic potential energy surfaces*

$$\epsilon_n[R] = \langle \psi_n | H_e | \psi_n \rangle \quad n = 0, 1, \dots \quad \epsilon_n \leq \epsilon_{n+1} \quad (2.7)$$

and *nonadiabatic couplings* (NACs), neglected in the BO approximation (yet of importance in many processes nevertheless^{40,41})

$$\tau_{nm}^\mu = \langle \psi_n | \partial_\mu \psi_m \rangle \quad n, m = 0, 1, 2, \dots \quad (2.8)$$

In these expressions, ψ_n is a normalized eigenstate of the time-independent electronic Hamiltonian. Since the electronic Hamiltonian depends on the position of the nuclei R , so do the eigenfunction ψ_n and eigenenergy ε_n . The NACs of eq 2.8 are defined in terms of the derivative $\partial_\mu \equiv \partial/\partial R_\mu$ with respect to one of the nuclear coordinates R_μ .

The ground-state adiabatic potential surface $\varepsilon_0[\mathbf{R}]$ can be calculated, often with very satisfactory success, using DFT. Because of the high efficiency of DFT applications, this allows scientists to explore with relatively high accuracy many molecular processes in detail. Such an approach is valid when it is possible to neglect electronic excitations (the BO approximation). Yet, in processes involving electronic excitations, other potential surfaces and, in particular, nonadiabatic couplings may be important. We discuss in this section how TDDFT can be used to calculate the excited potential surfaces $\varepsilon_n[\mathbf{R}]$ and the nonadiabatic couplings $\tau_{0n}[\mathbf{R}]$.

The NACs have several notable properties.^{13,42} τ^μ can be considered a real antisymmetric matrix. The sign of τ_{nm}^μ is arbitrary, although the signs of different components, for example, τ_{01}^μ and τ_{01}^{ν} , are related. The Epstein theorem holds⁴³

$$\tau_{nm}^\mu = \frac{\langle \psi_n | \partial_\mu H_e | \psi_m \rangle}{\varepsilon_m - \varepsilon_n} \quad (2.9)$$

showing that the BO approximation, where NACs are neglected, is invalid in regions where ε_n approaches ε_m . A particularly dramatic and widespread situation is the presence of conical intersections of potential energy surfaces at which the NACs are singular.^{14,42,44}

In order to compute NACs relating the ground-state ψ_0 and an excited-state ψ_n we use eq 2.9 which shows the NACs can be computed by simultaneously estimating the matrix element of the force operator $\langle \psi_0 | \partial_\mu H_e | \psi_n \rangle$ and the excitation energy $\omega_{n0} = \varepsilon_n - \varepsilon_0$. This last quantity also allows us to compute the excited-state potential.

We take the molecule in its ground-state at position \mathbf{R} and perturb it with a weak, short time-dependent pulse, as described in the previous section. The nuclear positions are clamped throughout the calculation.

In the previous section (eq 2.5), we considered a signal $\Delta Y(t)$ resulting from a perturbation caused by a weak field coupling to an operator $\pi(\hat{\mathbf{f}})$. For a signal of length T , the Gaussian-windowed Fourier-transformed quantity

$$\Delta \tilde{Y}(\omega) = \int e^{i\omega t} e^{-\frac{(t-T/2)^2}{2\sigma^2}} \Delta Y(t) dt$$

has peaks near the excitation energies given by⁴⁶

$$\Delta \tilde{Y}(\omega) \approx Q(\omega, \omega_{n0}) Y_{0n} \pi_{n0} \quad (2.10)$$

where

$$Q(\omega, \omega_{n0}) = \frac{2\pi\eta T\sigma}{i\hbar} e^{i\omega_{n0}T_0} \times e^{-\frac{T^2\omega_{n0}^2}{2}} e^{i(\omega-\omega_{n0})T_0} e^{-\frac{\sigma^2(\omega-\omega_{n0})^2}{2}} \quad (2.11)$$

Here σ is the size of the Gaussian window applied to the signal $\Delta Y(t)$. Equation 2.11 is exact in the limit of a long signal ($\sigma \rightarrow \infty$).

We use eq 2.10 twice. Once, taking $\hat{Y} = \hat{\pi}$ ($\hat{\pi}$ can be any operator having non-vanishing matrix elements between the ground state and the state n), $\Delta\tilde{\pi}(\omega) = Q(\omega, \omega_{n0}) |\pi_{n0}|^2$, and once taking for \hat{Y} the nuclear force: $y(\mathbf{r}) = F_\mu(\mathbf{r}) = -\partial_\mu V(\mathbf{r})$. Then, from eq 2.10 $\Delta\tilde{F}_\mu(\omega)/\omega_{n0} = -Q(\omega, \omega_{n0}) \tau_{0n}^\mu \pi_{n0}$, which upon squaring and dividing by $\Delta\tilde{\pi}(\omega)$ yields

$$|\tau_{0n}^\mu|^2 = \frac{|\Delta\tilde{F}_\mu(\omega)|^2}{\omega_{n0}^2 Q(\omega, \omega_{n0})^* \Delta\tilde{\pi}(\omega)} \quad (2.12)$$

In applying this equation, one can determine ω accurately by searching for an appropriate value that renders $|\tau_{0n}^\mu|^2$ real.

We demonstrated the method on the H+H₂ system. For the application details, we refer the reader to ref 46. We used a cubic box of length $16a_0$, and grid-spacing $\Delta x = 0.5 a_0$. The time propagation was done in this case using the Chebyshev collocation.^{29,47} The adiabatic surfaces are shown in Fig. 2. As the conical intersection is approached the time-dependent calculation loses accuracy. This might result from the finite propagation time

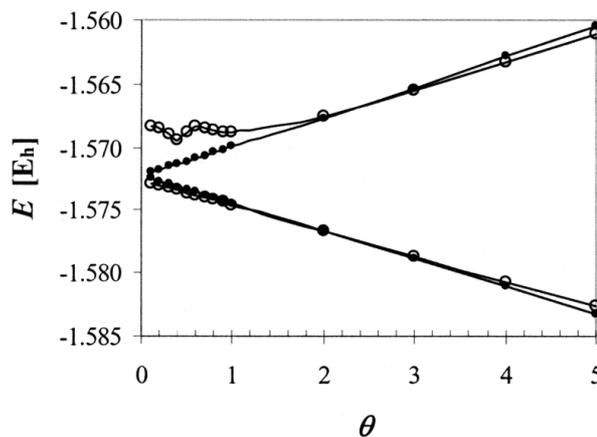


Fig. 2. The two adiabatic potential energy curves, as a function of the hyper-spherical angle θ , computed by DFT/TDDFT (empty circles) and by Abrol et al.⁴⁵ (filled circles). For $\theta > 1$ the agreement is very good. However, as the CI is approached even closer, the ALDA results fail to show the crossing. From ref 46, with permission from Elsevier.

and the small energy gap. In Fig. 3 we present the calculated two in-plane components of the NACs for fixed hyperspherical coordinates $\rho = 2.5 a_0$ and $\phi = 120^\circ$, as a function of θ (here, we refer the reader to ref 45 for explanation of the coordinates nomenclature). For $\theta > 1$ the agreement between the DFT and CASSCF calculations is quantitatively good. The energetics is also very close.

C. Nuclear Dynamics Near Metallic Clusters

As the final application of TDDFT we discuss the nuclear dynamics near a metal cluster. Metallic systems are characterized by a set of closely spaced energy levels. Thus, the adiabatic surfaces governing the motion of an atom close to the surface of a metal cluster are very dense and it is expected that they are parallel. The nuclear dynamics near such a surface can relatively easily excite electrons in the metal (NACs of eq 2.9 are relatively large because energy spacing is small). This observation is often used to justify the “friction approximation”, assuming that the nuclear motion is well approximated as motion on the lowest adiabatic state with an appropriate friction constant.^{48,49} Friction is a manifestation of the loss of nuclear kinetic energy to the creation of electron–hole pairs, i.e., electronic excitations, in the metal. The friction constant can be calculated from the force–force correlation function⁴⁹. Such a calculation for the case of a hydrogen atom near a copper surface has been performed using TDDFT recently.^{50,51}

The applicability of the friction theory has not been

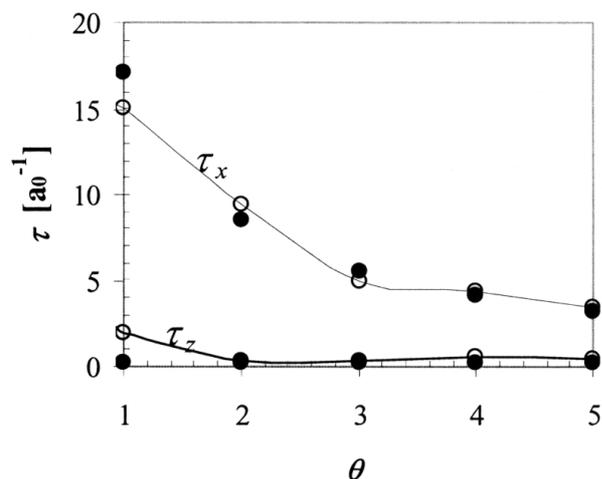


Fig. 3. The Cartesian components of the NACs as a function of the hyperspherical angle q , computed using TDDFT (empty circles) and by Abrol et al.⁴⁵ (filled circles). The agreement is good for $q > 1$. For $q < 1$ (not shown) ALDA rapidly loses accuracy. From ref 46, with permission from Elsevier.

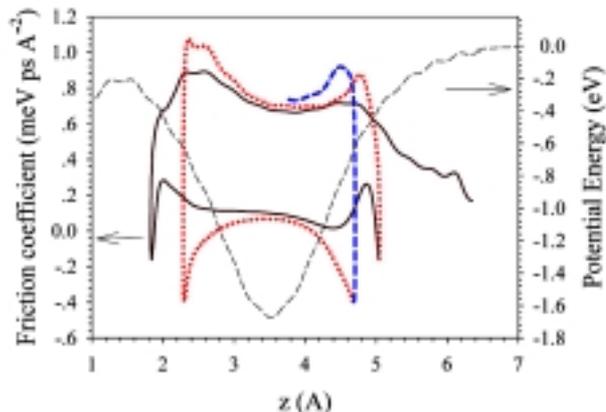


Fig. 4. The effective friction coefficient along the nuclear trajectory. First round (full), second round (dotted) and beginning of third round (dashed), superimposed—the adiabatic potential (dash-dotted).

thoroughly tested by comparing it to a more rigorous approach. In this section we test this theory on the collision of a hydrogen atom with a metal cluster. The cluster is modeled by a jellium ball of radius $\sim 3 \text{ \AA}$ containing 19 electrons. The dynamics is studied by using the Ehrenfest molecular dynamics approximation. Here the hydrogen nucleus moves classically under the *average* force exerted by all the electrons. The deviance of this average force from the “adiabatic force”, i.e., the force derived from the ground-state potential energy curve, is then interpreted as a friction force. Using the instantaneous velocity of the hydrogen atom, the instantaneous friction coefficient can be calculated. The details of the theory and the calculation are described in ref 52.

The friction coefficient we find is displayed in Fig. 4. It shows an unexpected behavior: the “friction” coefficient operating on the atom as it approaches the surface is different than when it recedes. A possible explanation for this is that the excited potential surfaces are *not* parallel to the ground state, as is often assumed. Thus, the nonadiabatic force cannot be interpreted as pure friction. Some of it is due to the conservative adiabatic forces on the excited states. We are currently in the process of proving this explanation.

3. MEMORY EFFECTS

Almost all functionals of TDDFT are “memory-less”, in that the exchange correlation potentials $v_{xc}(\mathbf{r}, t)$ depend on the electronic density at $n(\mathbf{r}', t)$. In fact, a more rigorous approach should exhibit dependence on $n(\mathbf{r}, t')$ where $t' < t$. Such a dependence is called memory. It is

known that ignoring memory can lead to errors in excited states that have a double excitation character.⁵³ Furthermore, it is expected that memory effects are important in the description of molecular interactions with strong fields.

The inclusion of memory effects in TDDFT is complicated because the resulting potentials must ensure compliance with Galilean invariance,^{54,55} namely that at each instant t

$$\begin{aligned} \int n(\mathbf{r}, t) \nabla v_{XC}(\mathbf{r}, t) d^3r &= 0 \\ \int n(\mathbf{r}, t) \mathbf{r} \times \nabla v_{XC}(\mathbf{r}, t) d^3r &= 0 \end{aligned} \quad (3.1)$$

These relations are a consequence of the fact that the total force and torque exerted by the electrons upon themselves must be zero. It is shown⁵⁶ that these requirements complicate TDDFT to the extent that the theory must be generalized so that the main variable is not the electronic density, but the current density $\mathbf{j}(\mathbf{r}, t)$. This leads to the time-dependent current-density functional theory (TDCDFT). The structure of TDCDFT is similar to TDDFT, with the essential difference that the Kohn–Sham equations now include an exchange–correlation vector potential \mathbf{A}_{XC}

$$i\dot{\phi}_q(\mathbf{r}, t) = -\frac{1}{2}(\nabla + \mathbf{A}_{XC})^2 \phi_q(\mathbf{r}, t) + v_s(\mathbf{r}) \phi_q(\mathbf{r}, t) \quad (3.2)$$

Information from the dynamical behavior of the homogeneous electron gas has been used⁵⁶ to construct a XC vector potential that leads within linear response theory to compliance with the zero-force and zero-torque.

There has been some recent progress in determining functionals that allow going beyond linear response.^{57–59} We have recently shown a way to derive Galilean invariant potentials.⁶⁰ The theory is formulated using Lagrangian coordinates. We view the electrons as a fluid having a velocity field $\mathbf{u}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t)/n(\mathbf{r}, t)$. At time $t = 0$ we divide the fluid to small parcels, each parcel identified by its position \mathbf{r} at $t = 0$. As the electrons move about, each fluid parcel moves to the position $\mathbf{R}(\mathbf{r}, t)$. The trajectory function is determined from the equation $\dot{\mathbf{R}}(\mathbf{r}, t) = \mathbf{u}(\mathbf{R}(\mathbf{r}, t), t)$. The function $\mathbf{R}(\mathbf{r}, t)$ is a Lagrangian–Eulerian transformation (ELT). The coordinates \mathbf{R} (Eulerian) identify the fluid element by its position at time t while the coordinates \mathbf{r} identify the parcel by its position at time $t = 0$. The Jacobian of the ELT transformation is

$$\mathfrak{S}_{ij} = \partial_j R_i(\mathbf{r}, t) \quad (3.3)$$

where $i, j = 1, 2, 3$ designate the Cartesian components of the relevant vectors. Using the Jacobian, one can form

the ELT metric

$$\tilde{g}(\mathbf{r}, t) = \mathfrak{S}(\mathbf{r}, t)^T \mathfrak{S}(\mathbf{r}, t) \quad (3.4)$$

In principle, the XC potentials depend functionally on the current density \mathbf{j} . We indicate this as $v_{XC}[\mathbf{j}]$ and $\mathbf{A}_{XC}[\mathbf{j}]$. However, it can be shown,⁶⁰ that if this functional dependence is forced to be *through* the ELT, i.e., if $v_{XC}[\mathbf{j}] = w[\tilde{g}[\mathbf{j}]]$ for some functional w (and similar relation for \mathbf{A}_{XC}), then eqs. 3.1 are *automatically obeyed*. This has allowed us to write down quite general forms for the XC potentials, which can be parametrized, according to information taken from the dynamical properties of the homogeneous gas.⁵⁸

4. SUMMARY

We have given a short review of time-dependent density functional methods and presented several applications using this theory, which demonstrate the generality, potential, and power of the methods. We briefly discussed also the issue of memory effects in time-dependent current-density functional theory. Perhaps the most attractive feature of this emerging method is its ability to include much of the correct physics while maintaining simplicity and its broad generality. This has allowed application of the theory for a variety of different processes including study of electronic transport and conductance^{61,62} and strong-laser–molecular interactions.⁶³ The power of TDDFT extends beyond that shown here. For example, it has been shown capable of generating C_6 van der Waals coefficients with good approximation.⁶⁴

Current approximations of TDDFT not only suffer from lack of proper memory functionals. They also inherit some of the weaknesses of DFT. Despite their great success, present DFT functionals fail to account for anions and processes involving long-range charge transfer. For example, the polarizability of elongated molecules is strongly exaggerated.⁶⁵ These problems are associated with the existence of self-interaction in the local functionals,^{5,66–69} and exchange–correlation (XC) potentials derived from them exhibit spurious exponential decay at large distances from the molecule or solid surface.^{5,70} The self-interaction problem has recently been shown to strongly affect the quality of TDDFT excitation energies.⁶⁸ Recently, we have developed a DFT functional that does not suffer from long-range self-repulsion.⁹ This functional cures many of the illnesses in local DFT functionals. It is currently being tested also within a TDDFT framework and is seen to improve excitation energies of molecules as well.

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