VOL NUMBER 914/ISSUES 1–3 30 NOVEMBER 2009 ISSN 0166-1280
Vol. 914 is complete in one issue

ELSEVIER

JOURNAL OF MOLECULAR STRUCTURE

THEOCHEM
Theory and Modelling in Chemistry

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SPECIAL ISSUE
Time-dependent density-functional theory
for molecules and molecular solids

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Review

Time-dependent density-functional theory for molecules and molecular solids

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A B S T R A C T

Time-dependent density-functional theory (TDDFT) has become a well-established part of the modern theoretical chemist's toolbox for treating electronic excited states. Yet, though applications of TDDFT abound in quantum chemistry, review articles specifically focusing on TDDFT for chemical applications are relatively rare. This article helps to fill the void by first giving a historical review of TDDFT, with emphasis on molecular excitations and aspects of TDDFT which are important for quantum chemical applications, followed by a discussion of some modern evolutions with emphasis on the articles in this volume, and ending with a few thoughts about the future of TDDFT.

1. Introduction

The classic density-functional theory (DFT) of Hohenberg and Kohn [1] and Kohn and Sham [2] has become remarkably popular in recent years, almost completely replacing the Hartree-Fock method except when post-Hartree-Fock correlated methods are desired. Despite this success, conventional DFT has its limitations, one of which is fundamental and so independent of improvements in functionals. Conventional DFT is a static ground-state theory and hence is neither formally appropriate for handling time-dependent phenomena nor for handling excited states (though one can argue that the lowest excited state of a given symmetry might still be reasonably described in practice with conventional DFT.) This would unfortunately seem to exclude many interesting problems in the design of optical materials, in spectroscopy, and in photochemistry. Time-dependent DFT (TDDFT) provides an answer to these problems by beginning anew, but nevertheless managing to maintain strong parallels with conventional static ground-state DFT. Indeed the first application of TDDFT [3] simply *assumed* that DFT could be extended to handle time-dependent problems. Nevertheless the results were remarkable and the computational simplifications provided by replacing the Hartree-Fock exchange operator with a local multiplicative operator were highly attractive. Four years later, Runge and Gross [4] presented time-dependent analogues of the Hohenberg and Kohn theorems and of the Kohn and Sham approach of conventional DFT. With the advent of a linear response formulation for calculating excitation spectra which could be relatively easily implemented in existant Quantum Chemistry codes [5], applications of TDDFT rapidly took off. In fact,

a simple review of the literature reveals that TDDFT has now become the predominant single-reference theory for modeling the excited states of medium-sized and large molecules, and is apparently more frequently used then its natural competitors [i.e., configuration interaction singles (CIS) and complete active space plus second-order perturbation theory (CASPT2).] The objective of this "viewpoint paper" is to provide a brief historical review of TDDFT which I hope will provide added value to the other articles in this volume. This review is by no means unique as other reviews [6,7,5,8–21] and a couple of books [22,23] and even another Special Issue [24] on TDDFT have already appeared. But relatively few of these are written from the point of view of chemical applications and the present review helps to make this volume a bit more "self-contained," and hence more accessible for those seeking greater familiarity with TDDFT. Indeed this paper is intended to provide both background material and also attempts to situate the other articles in the context of modern applications of TDDFT to physical chemistry/chemical physics. It is inevitable that such an article will show some personal biases and this is all the more true in the final section where I try to do a bit of "crystal ball gazing" and speculate about future developments in TDDFT. Nevertheless I trust that this article will be useful and I hope that it will be as enjoyable to read as it was to write.

2. Brief history of TDDFT

2.1. DFT

The natural precursor of TDDFT is DFT. According to the Hohenberg–Kohn theorems [1], the total energy, E, and charge density, ρ, of N electrons in the presence of an external potential, v_{ext}

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(typically representing the electric field of the nuclei and any applied electric fields), is obtained by minimizing a functional (i.e., a function of a function),

$$E[\rho] = F[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}. \tag{II.1}$$

In the Kohn–Sham formulation of DFT [2], the density is expressed in terms of N orthonormal orbitals,

$$\rho(\mathbf{r}) = \sum_p n_p \mid \psi_p(\mathbf{r})\mid^2, \tag{II.2}$$

with occupations, n_p, equal to zero or one, and the universal (i.e., v_{ext}-independent) functional,

$$F[\rho] = -\frac{1}{2}\sum_p n_p \langle \psi_p \mid \nabla^2 \mid \psi_p \rangle + E_H[\rho] + E_{xc}[\rho], \tag{II.3}$$

where the Hartree (or classical Coulomb) energy is given by,

$$E_H[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1 d\mathbf{r}_2. \tag{II.4}$$

(Hartree atomic units are used throughout: $\hbar = m_e = e = 1$.) Here $E_{xc}[\rho]$ is the exchange-correlation (xc) energy functional. Minimizing the energy gives the Kohn–Sham equation,

$$\hat{h}_s[\rho]\psi_p(\mathbf{r}) = \epsilon_p\psi_p(\mathbf{r}), \tag{II.5}$$

where the single-particle Kohn–Sham hamiltonian is,

$$\hat{h}_s[\rho] = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}). \tag{II.6}$$

Here the Hartree potential,

$$v_H[\rho](\mathbf{r}_1) = \frac{\delta E_H[\rho]}{\delta\rho(\mathbf{r}_1)} = \int \frac{\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_2, \tag{II.7}$$

and the xc potential,

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}. \tag{II.8}$$

Since no practical exact form of the xc functional is known, this functional is approximated in practice. Once an xc approximation is chosen, the equations are to be solved self-consistently.

Improvements in functionals come in two different but complementary ways. One is to make the functional form more exact without changing the variables on which the functional depends. The other approach is to increase the number of variables on which

Table 1
Jacob's ladder for functionals [25]. (An updated version is given in Ref. [26].) Spin indices have been dropped for simplicity, however present practice is to always use spin-density functional theory where the density is a two-component object, $(\rho_\alpha, \rho_\beta)$. In noncollinear spin-density functional theory, the density may even have a four-components, $(\rho_{\alpha\alpha}, \rho_{\alpha\beta}, \rho_{\beta\alpha}, \rho_{\beta\beta})$.

Quantum chemical heaven	
Double-hybrid	$\rho(\mathbf{r}), x(\mathbf{r}), \tau(\mathbf{r}), \psi_i(\mathbf{r}), \psi_a(\mathbf{r})$[h]
Hybrid	$\rho(\mathbf{r}), x(\mathbf{r}), \tau(\mathbf{r}), \psi_i(\mathbf{r})$[g]
mGGA[c]	$\rho(\mathbf{r}), x(\mathbf{r}), \tau(\mathbf{r})$[e], $\nabla^2\rho(\mathbf{r})$[f]
GGA[b]	$\rho(\mathbf{r}), x(\mathbf{r})$[d]
LDA[a]	$\rho(\mathbf{r})$
Hartree World	

[a] Local density approximation.
[b] Generalized gradient approximation.
[c] Meta generalized gradient approximation.
[d] The reduced gradient $x(\mathbf{r}) = \mid \vec{\nabla}\rho(\mathbf{r})\mid /\rho^{4/3}(\mathbf{r})$.
[e] The local kinetic energy $\tau(\mathbf{r}) = \sum_p n_p\psi_p(\mathbf{r})\nabla^2\psi_p(\mathbf{r})$.
[f] There is some indication that the local kinetic energy density $\tau(\mathbf{r})$ and the Laplacian of the charge density, $\nabla^2\rho(\mathbf{r})$, contain comparable information [27].
[g] Occupied orbitals.
[h] Unoccupied orbitals.

the functional depends. This latter approach consists of climbing the Jacob's ladder shown in Table 1. While adding more variables should, in principle, make it easier to design more reliably accurate functionals, all that is really guaranteed in climbing the ladder is that calculations will become more expensive. Hence it is also important to improve the functionals at the lower ends of the ladder. More will be said about functionals in the specific context of TDDFT.

2.2. Pragmatic beginnings

It was already mentioned that the external potential can include applied perturbations, such as an electric field, $\mathscr{E}\cdot\mathbf{r}$, so it makes sense to calculate *static* response properties within the framework of DFT. In a common terminology, dipole moments,

$$\mu_q = -\frac{\partial E}{\partial \mathscr{E}_q}, \tag{II.9}$$

are a first-order property, while dipole polarizabilities are a second-order property,

$$\alpha_{q,q'} = -\frac{\partial^2 E}{\partial \mathscr{E}_q \partial \mathscr{E}_{q'}}. \tag{II.10}$$

The small modification needed to calculate *dynamic* polarizabilities is then quite natural and this is how TDDFT first came into being.

One of the first implementations of DFT response theory to calculate static polarizabilities was in 1973 by Ahlberg and Goscinski [28] in the context of Xα theory. The first modern local density approximation (LDA) calculations of static dipole polarizabilities were carried out for atoms in 1980 by Stott and Zaremba using a Green's function approach [29] and by Mahan using the modified Sternheimer approach [30]. The motivation was purely algorithmic: the advantages over Hartree-Fock being that only local multiplicative potentials appear in the equation for the first-order response of the Kohn–Sham orbitals, $\delta\psi_p$,

$$\left(\epsilon_p - \hat{h}_s[\rho]\right)\delta\psi_p(\mathbf{r}) = v_{eff}(\mathbf{r})\psi_p(\mathbf{r}), \tag{II.11}$$

where the single-particle Kohn–Sham hamiltonian was defined in Eq. (II.6), and the effective potential, v_{eff}, is the sum of the applied potential, v_{appl}, and the first-order response of the self-consistent field (SCF),

$$\delta v_{SCF}[\rho](\mathbf{r}_1) = \int \left(\frac{1}{r_{12}} + f_{xc}[\rho](\mathbf{r}_1,\mathbf{r}_2)\right)\delta\rho(\mathbf{r}_2)\, d\mathbf{r}_2. \tag{II.12}$$

Here the xc-kernel is,

$$f_{xc}[\rho](\mathbf{r}_1,\mathbf{r}_2) = \frac{\delta v_{xc}[\rho](\mathbf{r}_1)}{\partial\rho(\mathbf{r}_2)} = \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}. \tag{II.13}$$

Since the linear-response of the charge density only involves the response of the occupied orbitals,

$$\delta\rho(\mathbf{r}) = 2\sum_p n_p\psi_p(\mathbf{r})\delta\psi_p(\mathbf{r}), \tag{II.14}$$

solving Eqs. (II.10)–(II.14) can be restricted to the self-consistent solution of N coupled equations. The Green's function approach of Stott and Zaremba [29] and the modified Sternheimer approach of Mahan are reviewed in the book of Mahan and Subbaswamy [22].

Once these methods are worked out, it is quite natural to extrapolate to the time domain in an *ad hoc* sort of way. Such an extrapolation was first carried out by Zangwill and Soven [3] giving us our first milestone in the history of TDDFT (Table 2). Zangwill and Soven began with a system consisting of N electrons in their ground stationary state and added a time-dependent perturbation. They assumed that the xc potential in the Kohn–Sham equation

Table 2
Some milestones in the history of TDDFT.

Year	Milestone
1980	First pragmatic application [3]
1984	Runge–Gross theorems [4]
1995	Casida's equations [5]
1996	Stability conditions [31]
	Rajagopal's causality solution [32]
1998	Exact exchange kernel [33]
	Rydberg excitations [34]
	Conducting polymers [35]
1999	Tamm–Dancoff approximation [36]
	Analytic derivatives [37]
2000	PCM solvent model [38]
2001	Keldysh action formalism [11]
2003	Charge-transfer excitations [39]
	Quadratic response theory [40]
	Spin-flip (hybrid functionals) [41]
2004	Double excitations [42]
	KSCED subsystem theory [43]
	Range-separated hybrids [44]
	Vibrational structure [45]
2005	Spin-flip (noncollinear) [46]
	Two-component ZORA [47,48]
	Mukamel's causality solution [49]
2008	Tully-like photodynamics [50]
	Runge–Gross–Vignale action principle [51]
	Excitation energy benchmark set [52,53]
2009	Spurious (?) excitations [54]

would react instantaneously and without memory to any temporal change of the charge density. This has come to be known in the TDDFT literature as the *adiabatic approximation*,

$$v_{xc}[\rho_t](\mathbf{r}, t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})},$$ (II.15)

where the important distinction has been made between $\rho_t(\mathbf{r})$ and $\rho(\mathbf{r}, t)$ which are the same *except* that ρ (i.e., $\rho(\mathbf{r}, t)$) is a function of $\mathbf{r} = (x, y, z)$ and of t, while ρ_t (i.e., $\rho_t(\mathbf{r})$) is considered as a distinct different function of $\mathbf{r} = (x, y, z)$ for each value of the parameter t. Within the adiabatic approximation, the time-dependent Kohn–Sham equation is

$$\hat{h}_s[\rho_t]\psi_p(\mathbf{r}, t) = i\frac{\partial \psi_p(\mathbf{r}, t)}{\partial t},$$ (II.16)

where,

$$\hat{h}_s[\rho_t] = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}, t) + v_H[\rho_t](\mathbf{r}, t) + v_{xc}[\rho_t](\mathbf{r}, t)$$ (II.17)

[Compare with Eqs. (II.5) and (II.6).] Although we are primarily concerned with linear response solutions of Eq. (II.16), it can also be solved by direct numerical integration in real time. The article by Roi Baer in this volume [55] discusses the extreme case of high-frequency large amplitude perturbations where he argues that the TDDFT adiabatic approximation will also be valid.

Let us return once again to the linear response problem to see how our basic equations change once time is introduced. The stationary state solutions have the form,

$$\psi_p(\mathbf{r}, t) = \psi_p(\mathbf{r})e^{-i\epsilon_p t}.$$ (II.18)

This is the solution at time $t = -\infty$ in the distant past when the time-dependent perturbation is gradually turned on so as to avoid transient solutions. This is generally referred to as adiabatic perturbation theory and constitutes the second use of the term "adiabatic" in this article. Note that a rigorous treatment involves exponential

convergence factors with infinitessimal factors (0^+) which assure that the time-dependent perturbation goes properly to zero in the distant past. The time evolution of the orbitals are now given by,

$$\left(\hat{h}_s[\rho(t)] + v_{appl}[\rho](\mathbf{r}, t)\right)\psi_p(\mathbf{r}, t) = i\frac{\partial \psi_p(\mathbf{r}, t)}{\partial t}.$$ (II.19)

Without loss of generality,

$$\psi_p(\mathbf{r}, t) = \left(\psi_p(\mathbf{r}) + \delta\psi_p(\mathbf{r}, t) + \cdots\right)e^{-i\epsilon_p t},$$ (II.20)

which allows us to deduce that the linear response of the ground state satisfies

$$v_{eff}[\rho](\mathbf{r}, t)\delta\psi_p(\mathbf{r}, t) = \left(i\hbar\frac{\partial}{\partial t} - \hat{h}_s[\rho_0] + \epsilon_p\right),$$ (II.21)

where $\rho_0 = \rho(t = -\infty)$ (i.e., before the perturbation is turned on) and the time-dependent effective potential, $v_{eff}[\rho_t](\mathbf{r}_1, t)$, is the sum of the time-dependent applied potential, $v_{appl}(\mathbf{r}_1, t)$, and the response of the SCF (a sort of reaction field),

$$\delta v_{SCF}[\rho_0](\mathbf{r}_1, t) = \int \left(\frac{1}{r_{12}} + f_{xc}[\rho_0](\mathbf{r}_1, \mathbf{r}_2)\right)\delta\rho(\mathbf{r}_2, t)\,d\mathbf{r}_2.$$ (II.22)

Fourier transforming leads to,

$$\left(\epsilon_p - \hat{h}_s[\rho_0] + \omega + i0^+\right)\delta\psi_p(\mathbf{r}, \omega) = v_{eff}[\rho](\mathbf{r}, \omega)\psi_p(\mathbf{r}).$$ (II.23)

The Fourier transform of the effective potential requires,

$$\delta\rho(\mathbf{r}, \omega) = \sum_p n_p \left(\psi_p(\mathbf{r})\delta\psi_p^*(\mathbf{r}, \omega) + \delta\psi_p(\mathbf{r}, \omega)\psi_p^*(\mathbf{r})\right)$$
$$= \sum_p n_p \left[\psi_p(\mathbf{r})\left(\delta\psi_p(\mathbf{r}, -\omega)\right)^* + \delta\psi_p(\mathbf{r}, \omega)\psi_p^*(\mathbf{r})\right],$$ (II.24)

so Eq. (II.23) must also be solved at negative frequencies. Thus only a small modification of the static response equations is actually needed to do dynamic response theory.

Interestingly TDDFT also appeared in the physics literature in a different context at about the same time as Zangwill and Soven's landmark work. During the 1970s and the beginning of the 1980s, Hanke and Sham were working on solving the Bethe–Salpeter equation for solids [56–59]. This involves calculating the time-dependent polarization propagator in a manner similar to TDDFT and one of the approximations which they considered was exactly TDDFT. In the late 1980s I was working on simplified Green's function approximations [60,61] and Hanke and Sham's work was a major inspiration for my taking an interest in TDDFT.

2.3. DFT analytic derivatives

Every quantum chemist should know about another application of static response theory. This is the calculation of analytic derivatives for the efficient obtention of the forces needed for *ab initio* dynamics and optimizations of geometries [62]. About 15 years after Zangwill and Soven's classic work, quantum chemists were still largely unaware of TDDFT, but they were working on second analytic derivatives for static ground state DFT. The resultant coupled perturbed Kohn–Sham (CPKS) equations [63–66] strongly resemble my formulation of linear-response TDDFT (LR-TDDFT) [5] which would appear later, and show the extent to which the quantum chemistry community was poised to incorporate these equations into their computer codes. Let us give a brief review of the CPKS method, whose goal is to evaluate derivatives with respect to a general parameter η. The most typical value for η is some geometrical coordinate so that derivatives are analytic gradients and hence provide forces for automatic geometry optimizations. However η could also refer to the magnitude of an applied electric

field, which gives a hint as to why CPKS may have something to do with a practical implementation of TDDFT (*vide infra*).

In quantum chemistry calculations, the molecular orbitals (MOs), ψ_s, are expanded in a basis of atomic orbitals (AOs), χ_μ:

$$\psi_s(\mathbf{r}) = \sum_\mu \chi_\mu(\mathbf{r}) c_{\mu,s}. \tag{II.25}$$

When the parameter η varies, the AOs, χ_μ, and the MO coefficients in the AO basis, $c_{\mu,s}$, both vary. We would like to separate these two types of η-dependent variations and, if possible, eliminate any derivatives with respect to the $c_{\mu,s}$ since these are costly to calculate. To carry out our program we develop,

$$\frac{\partial \psi_s(\mathbf{r})}{\partial \eta} = \psi_s^\eta(\mathbf{r}) + \sum_\mu \psi_r(\mathbf{r}) U_{r,s}^\eta. \tag{II.26}$$

In general, the superscript η is reserved for a derivative over AOs at constant $c_{\mu,s}$ giving so-called "core" or "skeleton" terms. So,

$$\psi_s^\eta(\mathbf{r}) = \sum_\mu \frac{\partial \chi_\mu(\mathbf{r})}{\partial \eta} c_{\mu,s}. \tag{II.27}$$

However an exception is the matrix $\mathbf{U}^\eta$ of coupled perturbed coefficients which is defined by,

$$\sum_v \chi_v(\mathbf{r}) \frac{\partial c_{v,s}}{\partial \eta} = \sum_r \psi_r(\mathbf{r}) U_{r,s}^\eta. \tag{II.28}$$

It follows that,

$$U_{r,s}^\eta = \sum_{\mu,v} c_{\mu,r}^* S_{\mu,v} \frac{\partial c_{v,s}}{\partial \eta}, \tag{II.29}$$

where,

$$S_{\mu,v} = \langle \chi_\mu \mid \chi_v \rangle, \tag{II.30}$$

is the AO overlap matrix. Taking the functional derivative of the MO orthonormality relation,

$$\delta_{r,s} = \langle \psi_r \mid \psi_s \rangle = \sum_{\mu,v} c_{\mu,r}^* S_{\mu,v} c_{v,s}, \tag{II.31}$$

leads to what I call the "turnover rule,"

$$U_{q,p}^{\eta,*} = -U_{p,q}^\eta - S_{p,q}^\eta. \tag{II.32}$$

For real coupled perturbed coefficients,

$$U_{p,p}^\eta = -\frac{1}{2} S_{p,p}^\eta. \tag{II.33}$$

It is now straightforward to take the derivative of the energy expression to obtain,

$$\frac{\partial E}{\partial \eta} = E^\eta - \sum_{\mu,v} S_{\mu,v}^\eta W_{v,\mu}, \tag{II.34}$$

where,

$$W_{\mu,v} = \sum_i c_{\mu,i} \epsilon_i n_i c_{v,i}^* \tag{II.35}$$

is the energy-weighted density matrix. The first term is the Hellmann–Feynman force. In wave function terms,

$$E^\eta = \langle \Psi \mid \frac{\partial \widehat{H}}{\partial \eta} \mid \Psi \rangle. \tag{II.36}$$

The second term is the Pulay force. It is there because the AOs move with the nuclei and it is necessary to ensure that the calculated forces are zero when the calculated energy is a minimum. Since the coupled perturbed coefficients do not enter into the calculation of the first analytic derivative, the calculation of this derivative is finally really relatively trivial.

Second analytical derivatives for the ground state require us to solve a coupled perturbed equation for the $U_{p,q}^\eta$. We find upon differentiating the MO eigencondition,

$$F_{p,q} = \delta_{p,q} \epsilon_q, \tag{II.37}$$

that,

$$\sum_{p',q'} \left(\delta_{p,p'} \delta_{q,q'} \frac{\epsilon_q - \epsilon_p}{n_q - n_p} + K_{pq,p'q'} \right) (n_{q'} - n_{p'}) U_{p',q'}^\eta$$
$$= F_{p,q}^\eta - S_{p,q}^\eta \epsilon_q - \sum K_{pq,p'q'} n_{p'} S_{p',q'}^\eta. \tag{II.38}$$

The coupling matrix is defined by,

$$K_{pq\sigma,rs\tau} = \frac{\partial v_{pq\sigma}^{SCF}}{\partial P_{rs\tau}} = \begin{cases} (pq \mid f_H \mid rs) - \delta_{\sigma,\tau}(pr \mid f_H \mid sq); & \text{HF} \\ (pq \mid f_H \mid rs) + (pq \mid f_{xc}^{\sigma,\tau} \mid rs); & \text{DFT} \end{cases}, \tag{II.39}$$

where the SCF was previously defined [Eq. (II.12)]. Naturally hybrid xc functionals require some combination of the pure DFT and HF formulae. Here

$$(pq \mid f \mid rs) = \int \int \psi_p^*(\mathbf{r}) \psi_q(\mathbf{r}) f(\mathbf{r},\mathbf{r}') \psi_r^*(\mathbf{r}') \psi_s(\mathbf{r}') \, d\mathbf{r} d\mathbf{r}', \tag{II.40}$$

where f can be either the Hartree kernel,

$$f_H(\mathbf{r}_1, \mathbf{r}_2) = 1/r_{12}, \tag{II.41}$$

or the xc-kernel, f_{xc} [Eq. (II.13)].

It is clear from the turnover rule that there are many linear-dependencies among the coupled perturbed coefficients. By working a little harder, we arrive at the equation,

$$\sum_{j,b} \mathscr{A}_{ai,bj} U_{bj}^\eta = \mathscr{B}_{ai}^0, \tag{II.42}$$

for the nonredundant coupled perturbed coefficients, where

$$\mathscr{A}_{ai,bj} = \delta_{i,j} \delta_{a,b} \frac{\epsilon_i - \epsilon_a}{n_i - n_a} - (K_{ai,jb} + K_{ai,bj})$$
$$\mathscr{B}_{ai}^0 = F_{ai}^\eta - S_{ai}^\eta \epsilon_i - \sum_{j,k} K_{ai,kj} S_{jk}^\eta, \tag{II.43}$$

and I am using the MO index convention,

$$\underbrace{abc \cdots fgh}_{\text{unoccupied}} \underbrace{ijklmn}_{\text{occupied}} \underbrace{opq \cdots xyz}_{\text{free}}. \tag{II.44}$$

The redundant coupled perturbed coefficients may be calculated from the nonredundant coefficients by using the expression,

$$U_{p,q}^\eta = \frac{1}{\epsilon_q - \epsilon_p} \left[F_{p,q}^\eta - S_{p,q}^\eta \epsilon_q - \sum_{j,k} K_{pq,jk} S_{jk}^\eta \right.$$
$$\left. + \sum_{j,b} (K_{pq,bj} + K_{pq,jb}) U_{bj}^\eta \right]. \tag{II.45}$$

We shall not pursue second-analytic derivatives for the ground state any further. This is enough to see the relation with static response theory. The response of the density matrix is given by,

$$\frac{\partial P_{q,p}}{\partial \eta} = U_{q,p}^\eta n_p + U_{p,q}^{\eta,*} n_q = U_{q,p}^\eta (n_p - n_q) - S_{q,p}^\eta n_q. \tag{II.46}$$

Applying this to the CPKS Eq. (II.38) gives,

$$\sum_{p',q'} \left(\delta_{p,p'} \delta_{q,q'} \frac{\epsilon_q - \epsilon_p}{n_q - n_p} + K_{pq,p'q'} \right) \frac{\partial P_{q',p'}}{\partial \eta} = F_{p,q}^\eta. \tag{II.47}$$

This last equation may be expressed as a matrix equation partitioned into two parts depending upon whether p is occupied and q is unoccupied ($\mathbf{X} = \partial \mathbf{P}/\partial \eta$) or vice versa ($\mathbf{Y} = \partial \mathbf{P}^*/\partial \eta$),

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \begin{pmatrix} \vec{F}^\eta \\ \vec{F}^{\eta*} \end{pmatrix}, \tag{II.48}$$

where the $\mathbf{A}$ and $\mathbf{B}$ matrices are defined by,

$$A_{ia,jb} = \delta_{i,j}\delta_{a,b}(\epsilon_a - \epsilon_i) + K_{ia,jb}$$
$$B_{ia,jb} = K_{ia,bj}. \tag{II.49}$$

Notice the distinction between $\mathbf{F}_I$ which is viewed as a matrix and $\vec{F}_I$ which is viewed as a column vector, but which are nevertheless the same quantity.

The $\mathbf{A}$ and $\mathbf{B}$ matrices also appear in the analysis of the stability of the ground state spin-restricted solution of the Kohn–Sham equation [31]. Briefly, we consider an arbitrary unitary transformation of the orbitals,

$$\psi_i^\lambda(\mathbf{r}) = \exp\left[i\lambda\left(\widehat{R} + i\widehat{I}\right)\right]\psi_i(\mathbf{r}), \tag{II.50}$$

where $\widehat{R}$ and $\widehat{I}$ are real operators, and ask if the energy is lowered [13]. The corresponding energy expression is,

$$E_\lambda = E_0 + \lambda^2\left[\vec{R}^\dagger(\mathbf{A} - \mathbf{B})\vec{R} + \vec{I}^\dagger(\mathbf{A} + \mathbf{B})\vec{I}\right] + \mathcal{O}(\lambda^3), \tag{II.51}$$

where matrix elements of the $\widehat{R}$ and $\widehat{I}$ operators have been arranged in column vectors and the $\mathcal{O}(\lambda)$ term disappears because the energy has already been minimized before considering symmetry breaking.

This is enough to see the relation with LR-TDDFT which will be presented a little later in this article. One reason that quantum chemists working on DFT analytic derivatives did not go further is that they were largely unaware of the formal justification of extending DFT into the time domain.

2.4. Establishing the formalism

Several attempts have been made in the past to extend DFT into the time domain [67–71], but it is the work of Runge and Gross [4] which provides the formal foundation of modern TDDFT. They presented two theorems (RG1 and RG2) analogous to the two Hohenberg–Kohn theorems (HK1 and HK2) [1].

The first theorem is fundamentally a theorem about the current density,

$$\mathbf{j}(\mathbf{r}_1, t) = N\Im m\left\{\int\int\cdots\int[\nabla_1\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N, t)]\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N, t) \\ \times d\sigma_1 d\mathbf{x}_2\cdots d\mathbf{x}_N\right\}, \tag{II.52}$$

where the N electron wave function satisfies the time-dependent Schrödinger equation,

$$\widehat{H}\Psi(t) = i\frac{\partial}{\partial t}\Psi(t). \tag{II.53}$$

The current density satisfies the continuity equation,

$$\frac{\partial\rho(\mathbf{r}, t)}{\partial t} + \nabla\cdot\mathbf{j}(\mathbf{r}, t) = 0. \tag{II.54}$$

In the case of a single-determinant wave function,

$$\mathbf{j}(\mathbf{r}, t) = \Im m\sum_{i=1,N}[\nabla\psi_i(\mathbf{r}, t)]\psi_i^*(\mathbf{r}, t). \tag{II.55}$$

RG1 states that the time-dependent charge-density and the initial wave function $\Psi_0 = \Psi(t = t_0)$ together determine the external potential up to an additive function of time:

$$v_{ext}(\mathbf{r}, t) + C(t) \leftarrow (\rho(\mathbf{r}, t), \Psi_0). \tag{II.56}$$

It is assumed that the external potential can be expressed as a Taylor series in time,

$$v_{ext}(\mathbf{r}, t) = \sum_{k=0}^\infty c_k(\mathbf{r})(t - t_0)^k, \tag{II.57}$$

with

$$c_k(\mathbf{r}) = (1/k!)\left[\partial^k v_{ext}(\mathbf{r}, t)/\partial t^k\right]_{t=t_0}. \tag{II.58}$$

Most physical potentials can be approximated arbitrarily closely by such a function. The equation of motion,

$$i\hbar\frac{\partial\langle\Psi(t)\,|\,\hat{j}_q\,|\,\Psi(t)\rangle}{\partial t} = \langle\Psi(t)\,|\,[\hat{j}_q, \widehat{H}(t)]\,|\,\Psi(t)\rangle, \tag{II.59}$$

is used to show that two external potentials generating the same current density cannot differ by more than an additive function of time. Then the continuity Eq. (II.54) is used to show from this result that two external potentials generating the same time-dependent charge density cannot differ by more than an additive function of time. This involves the vanishing of a certain integral over a boundary surface which will always be the case for normal electric fields generated by finite sets of charges. A corollary to RG1 is that the time-dependent charge density, $\rho(\mathbf{r}, t)$, and the initial wave function, Ψ_0 together fix the number of particles, N, and the external potential up to an arbitrary additive function of time, $v_{ext}(\mathbf{r}, t) + C(t)$. Hence $\rho(\mathbf{r}, t)$ and Ψ_0 determine the time-dependent hamiltonian up to an additive function of time:

$$\widehat{H}(t) + C(t) \leftarrow (\rho(\mathbf{r}, t), \Psi_0). \tag{II.60}$$

That means that the equation of motion for the wave function can always be integrated provided we know the initial wave function, Ψ_0, at time t_0 to obtain,

$$\Psi(t) = \Psi[\rho, \Psi_0](t)e^{i\phi(t)}. \tag{II.61}$$

where the phase factor is given by,

$$\phi(t) = \int_{t_0}^t C(t')\,dt'. \tag{II.62}$$

If our system is in its ground state at time t_0, then we can use HK1 to remove the dependence on Ψ_0 to obtain,

$$\Psi(t) = \Psi[\rho](t)e^{i\phi(t)}. \tag{II.63}$$

Thanks to RG1 we have that the external potential of the real system is a functional of the density. This is also true for the fictitious system of noninteracting electrons, so we can write down a time-dependent Kohn–Sham equation,

$$\left[-\frac{1}{2}\nabla_1^2 + v_{ext}(\mathbf{r}_1, t) + \int\frac{\rho(\mathbf{r}_2, t)}{r_{12}}\,d\mathbf{r}_2 + v_{xc}[\rho](\mathbf{r}_1, t)\right]\psi_p(\mathbf{r}_1, t) \\ = i\frac{\partial\psi_p(\mathbf{r}_1, t)}{\partial t}. \tag{II.64}$$

(Rajam, Hessler, Gaun, and Maitra in their paper in the present volume [72] use the more general formulation $v_{xc}[\rho, \Psi_0, \Phi_0]$ because they do not necessarily want to apply a time-dependent potential to a system in its ground stationary state.) For some people, RG1 is a sufficient argument. We do not need to express the TDDFT xc-potential as a functional derivative of anything at all for it to exist. On the other hand, we still need to find approximations for this quantity.

The goal of RG2 was to propose a stationary action principle in analogue to the variational principle of HK2. This will not be discussed here except to note that the Dirac–Frenkel action,

$$A = \int_{t_0}^{t_1}\langle\Psi(t')\,|\,i\hbar\frac{\partial}{\partial t'} - \widehat{H}(t')\,|\,\Psi(t')\rangle\,dt', \tag{II.65}$$

originally proposed by Runge and Gross appeared to be inadequate. It was replaced by Robert van Leeuwen with a more appropriate Keldysh action formalism [11]. Earlier Rajagopal had also suggested

an alternative action formalism, related to the Keldysh action, which allowed access to the Berry phase [32]. Mukamel proposed a different solution [49]. However Vignale has recently shown how the Runge–Gross stationary action principle can be rehabilitated by taking boundary conditions properly into account [51]. According to the Runge–Gross–Vignale action principle, instead of making the Dirac–Frenkel action [Eq. (II.65)] stationary ($\delta A = 0$), the variation of the action must coincide with the variation in the final time boundary condition,

$$\delta A[\rho, \Psi_0] = i \langle \Psi[\rho, \Psi_0](t_1) \mid \delta \Psi[\rho, \Psi_0](t_1) \rangle. \tag{II.66}$$

Not only does Vignale show that this restores causality but also that this new action principle often leads to the same conclusions as the original Runge–Gross action principle, hence justifying previous conclusions based upon the Runge–Gross action.

The subtleties of TDDFT are sometimes frustrating (Table 3). Moreover a healthy formal theory is one which is criticized, defended, and corrective changes made where necessary. Healthy discussions continue regarding the validity of the formal foundations of TDDFT [73–75].

Almost all applications of TDDFT make the adiabatic approximation which assumes that the xc-potential reacts instantaneously and without memory to any temporal change in the charge density. Only a little is known about how to go beyond the adiabatic approximation. An early attempt was made by Kohn and Gross [76]. Dobson has proven that the xc-potential must obey a certain harmonic potential theorem [77]. Kurzweil and Baer have worked on developing xc-potentials with memory [78–81]. Perhaps the most successful approach to date has been the Vignale–Gross formalism which includes nonadiabatic effects through the current density [82,83]. Another approach involves a comoving Lagrangian reference frame [84]. More recently work has been carried out to extract the nonadiabatic behavior of the xc-kernel from the Bethe–Salpeter equation via a polarization propagator formalism or using related approaches [33,42,85–91].

2.5. Quantum chemistry technology

In the mid-1990s quantum chemistry was poised to implement TDDFT. It is difficult to look back and see things as they were at the time, but let us try. As the result of initial enthusiasm over the Xα method in the 1970s which turned sour as problem after problem were discovered, the *ab initio* community (i.e., quantum chemists using first-principles methods typically based upon the Hartree-Fock approximation as starting point) largely held DFT in contempt. But somehow density functional theorists (DFTists) managed to hang on as a separate parallel quantum chemistry community because of the great practical utility of their approach. The divide between these two communities finally broke down in the early 1990s, due in no small part to the efforts of Axel Becke who showed that many of the previous problems with Xα were due to the numerical implementations used, rather than the method itself, and to his development of improved functionals able to obtain significantly better bonding energies. Even while DFT was being redefined (Table 3), it was still widely regarded by *ab initio*-ists as a firmly grounded principle that DFT could not handle excited states. DFT methods were being developed specifically for

excited states [92], but it was TDDFT which was to finally provide the most popular DFT route to excited states [5,93]. Today typical modern quantum chemistry practice is to use DFT where once Hartree-Fock (HF) was used to model the energy landscape and electronic properties of chemical systems, only carrying out HF calculations when needed as a starting point for sophisticated and costly *ab initio* many-body calculations. Moreover time-dependent DFT (TDDFT) has become, with few exceptions, the primary single-reference method for treating excited states in medium and large sized molecules, leading to a veritable explosion of publications over the past decade.

A key step in bringing TDDFT to the quantum chemistry community was taken in 1995 when I wrote a review article on TDDFT [5] in which I reformulated LR-TDDFT to look like the standard implementation of LR-TDHF already available in most quantum chemistry codes. My article showed DFTists how configuration interaction-like equations arise naturally out of TDDFT and it explained to *ab initio*-ists the nature of TDDFT. The article spread rapidly in preprint form and lead to the implementation of what are sometimes referred to as "Casida's equations" in several different codes. I considered an N-electron system, initially in its ground stationary state, exposed to a time-dependent perturbation which was turned on adiabatically beginning at time $t = -\infty$, and deduced an equation for the dynamic response of the Kohn–Sham density matrix to the perturbation. The resultant dynamic equation,

$$\left\{ \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \right\} \begin{pmatrix} \delta \vec{P}(\omega) \\ \delta \vec{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \vec{v}_{\text{appl}}(\omega) \\ \vec{v}^*_{\text{appl}}(\omega) \end{pmatrix}, \tag{II.67}$$

includes the previously mentioned static equation [Eq. (II.48)] as a special case. Excitation energies and oscillator strengths can be extracted by rearranging this expression to take the form of the dynamic polarizability and using the sum-over-states theorem of optical physics,

$$\alpha(\omega) = \sum_{I \neq 0} \frac{f_I}{\omega_I^2 - \omega^2}, \tag{II.68}$$

where,

$$f_I = \frac{2}{3} \omega_I \sum_{q=x,y,z} \mid \langle \Psi_0 \mid q \mid \Psi_I \rangle \mid^2, \tag{II.69}$$

is the oscillator strength associated with the excitation energy,

$$\hbar \omega_I = E_I - E_0 \tag{II.70}$$

($\hbar = 1$ since we are using atomic units), and Ψ_0 and Ψ_I refer, respectively, to the ground and excited stationary states. It is enough for present purposes to recognize that the dynamic response of the density matrix, $\delta \vec{P}(\omega)$, must be infinite even for a perturbation, $\vec{v}_{\text{appl}}(\omega)$, arbitrarily small in magnitude, when the exciting frequency hits a resonance capable of exciting an electron. At such frequencies, Eq. (II.67) takes the form,

$$(\mathbf{x})(+\infty) = \mathbf{0}, \tag{II.71}$$

where x must be zero. This leads to the matrix pseudo-eigenvalue problem,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix}. \tag{II.72}$$

(An alternative derivation is possible using the techniques discussed in Ref. [94] of this volume.) This equation has paired excitation ($\omega_I > 0$) and de-excitation solutions ($\omega_I < 0$) which differ only by the interchange of $\mathbf{X}$ and $\mathbf{Y}$. The usual normalization is,

$$\vec{X}_I^\dagger \vec{X}_I - \vec{Y}_I^\dagger \vec{Y}_I = \begin{cases} +1; & \omega_I > 0 \\ -1; & \omega_I < 0 \end{cases}. \tag{II.73}$$

Table 3
Alternative interpretations of some popular acronyms.

Darned **F**ine Theory[a]
Terribly **D**ifficult **D**arned **F**ine Theory[b]

[a] Coined by Malcolm L.H. Green in connection with the impressive success of DFT in modeling inorganic chemistry.
[b] Coined by André Bandrauk in connection with applying TDDFT to coherent control.

The manner in which the pseudo-eigenvalue problem (II.73) is derived suggests that only those excitations with nonzero transition densities will be correctly described by TDDFT. This point has been emphasized recently by Heßelmann and Görling who refer to excitations with zero transition densities as "spurious" [54]. The $^1\Sigma_u^-(\pi \to \pi^*)$ transition in N_2 is an example of just such a spurious excitation and hence need not be correctly described by TDDFT. In fact, both the triplet and singlet $\Sigma_u^-(\pi \to \pi^*)$ transitions in N_2 are just given by the orbital energy difference in TDDFT which happens to be within 0.3 eV of the experimental values for the excitations [95]. Interestingly the triplet and singlet $\Sigma_u^-(\pi \to \pi^*)$ transitions in N_2 also have identical energies at the time-dependent Hartree-Fock level, though not using post-Hartree-Fock correlated methods and not experimentally [95]. Hirata and Head-Gordon introduced the Tamm–Dancoff approximation (TDA) to Eq. (II.72). This consists of neglecting the $\mathbf{B}$ matrices and simply solving,

$$\mathbf{A}\vec{X}_I = \omega_I \vec{X}_I. \tag{II.74}$$

Besides being computationally somewhat simpler than solving the full Eq. (II.72), the TDA has two additional advantages which are particularly clear in the case of LR-TDHF where the TDA gives configuration interaction singles (CIS). The first advantage in the CIS case is that there is a clear wave function,

$$\Psi_I = \sum_{i,a} \Phi_i^a X_{ia}^I, \tag{II.75}$$

where Φ_i^a is the ground-state determinant with an electron promoted from orbital ψ_i to orbital ψ_a. This means that excited-state expectation values are easily calculated in terms of the reduced difference density matrix (RDDM),

$$\Delta \mathbf{P}_I = \mathbf{P}_I - \mathbf{P}_0 = \frac{\mathbf{X}_I^\dagger \mathbf{X}_I - \mathbf{X}_I \mathbf{X}_I^\dagger}{\vec{X}_I^\dagger \vec{X}_I}, \tag{II.76}$$

a formula worked out by Maurice and Head-Gordon in the case of CIS [96]. The second advantage of the TDA follows from the stability condition (II.51), a detailed analysis of which shows the appearance of imaginary triplet excitation energies when the symmetry broken solution becomes lower in energy than the symmetry unbroken solution for the ground state. While this should not happen for the exact xc functional, it does happen in practice when approximate functionals are used. In this case the TDA decouples the excited-state problem from the ground-state stability problem and leads to markedly improved TDDFT potential energy surfaces [97–100]. This latter fact often makes the Tamm–Dancoff "approximation" *superior* to the original theory for certain types of chemical applications.

It is also possible to reduce the exact Eq. (II.72) to a matrix equation of the same dimension as the TDA equation without making approximations, provided we restrict ourselves to the first two rungs of Jacob's ladder (Table 1). For these functionals, the matrix

$$[\mathbf{A} - \mathbf{B}]_{ia,jb} = \delta_{i,j}\delta_{a,b}(\epsilon_a - \epsilon_i) \tag{II.77}$$

is easily invertible. For this reason, it is convenient to reformulate Eq. (II.72) as,

$$\mathbf{\Omega}\vec{F}_I = \omega_I^2 \vec{F}_I, \tag{II.78}$$

where,

$$\mathbf{\Omega} = (\mathbf{A} - \mathbf{B})^{+1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{+1/2}$$
$$\vec{F}_I = (\mathbf{A} - \mathbf{B})^{-1/2}\left(\vec{X}_I + \vec{Y}_I\right). \tag{II.79}$$

Consequently,

$$\vec{X}_I + \vec{Y}_I = (\mathbf{A} - \mathbf{B})^{+1/2}\vec{F}_I$$
$$\vec{X}_I - \vec{Y}_I = \omega_I(\mathbf{A} - \mathbf{B})^{-1/2}\vec{F}_I. \tag{II.80}$$

The transition matrix elements of an arbitrary local multiplicative one-electron operator, $\hat{x}$, are calculated as,

$$\langle \Psi_0 \mid \hat{x} \mid \Psi_I \rangle = \left(\omega_I \vec{F}_I^\dagger \vec{F}_I\right)^{-1/2} \vec{x}^\dagger (\mathbf{A} - \mathbf{B})^{1/2}\vec{F}_I. \tag{II.81}$$

The question arose as to how to assign excited states calculated within this formalism. I called this the TDDFT "assignment problem" [88] and suggested that the singly-excited parts of the configuration interaction coefficients of Ψ_I could be extracted as,

$$\vec{C}_I = \left(\omega_I \vec{F}_I^\dagger \vec{F}_I\right)^{-1/2}(\mathbf{A} - \mathbf{B})^{+1/2}\vec{F}_I$$
$$= \left[\left(\vec{X}_I + \vec{Y}_I\right)^\dagger \left(\vec{X}_I - \vec{Y}_I\right)\right]^{-1/2}\left(\vec{X}_I + \vec{Y}_I\right), \tag{II.82}$$

in analogy with the formula for transition matrix elements [Eq. (II.81)]. The corresponding RDDM is then,

$$\Delta \mathbf{P}_I = \frac{(\mathbf{X}_I + \mathbf{Y}_I)(\mathbf{X}_I + \mathbf{Y}_I)^\dagger - (\mathbf{X}_I + \mathbf{Y}_I)^\dagger(\mathbf{X}_I + \mathbf{Y}_I)}{\left(\vec{X}_I + \vec{Y}_I\right)^\dagger \left(\vec{X}_I - \vec{Y}_I\right)}. \tag{II.83}$$

In practice, the symmetry of the excited state is often already reflected in $\vec{F}_I$.

A more sophisticated formula for the TDDFT RDDM appears in the article of Ipatov, Cordova, Joubert Doriol, and Casida in this volume [101]. This is Rowe's formula, which may be obtained by an unrelaxed analytic derivative method applied to the analogous LR-TDHF equations,

$$\Delta \mathbf{P}_I = \frac{(\mathbf{X}_I \mathbf{X}_I^\dagger + \mathbf{Y}_I \mathbf{Y}_I^\dagger) - (\mathbf{X}_I^\dagger \mathbf{X}_I + \mathbf{Y}_I^\dagger \mathbf{Y}_I)}{\vec{X}_I^\dagger \vec{X}_I - \vec{Y}_I^\dagger \vec{Y}_I}$$
$$= \left[(\mathbf{X}_I + \mathbf{Y}_I)(\mathbf{X}_I + \mathbf{Y}_I)^\dagger - (\mathbf{X}_I + \mathbf{Y}_I)^\dagger(\mathbf{X}_I + \mathbf{Y}_I) + (\mathbf{X}_I - \mathbf{Y}_I)(\mathbf{X}_I - \mathbf{Y}_I)^\dagger\right.$$
$$\left. - (\mathbf{X}_I - \mathbf{Y}_I)^\dagger(\mathbf{X}_I - \mathbf{Y}_I)\right] \Big/ \left[\left(\vec{X}_I + \vec{Y}_I\right)^\dagger \left(\vec{X}_I - \vec{Y}_I\right) + \left(\vec{X}_I - \vec{Y}_I\right)^\dagger \left(\vec{X}_I + \vec{Y}_I\right)\right]. \tag{II.84}$$

In interpreting this equation, it must be kept in mind that it simultaneously describes excitations and de-excitations,

$$\Delta \mathbf{P}_I = \begin{cases} \mathbf{P}_I - \mathbf{P}_0; & \text{excitation} \\ \mathbf{P}_0 - \mathbf{P}_I; & \text{de-excitation} \end{cases}, \tag{II.85}$$

which explains the signs in Eq. (II.84). In fact, Rowe's formula may be regarded as "just" a sort of symmetrized form of Eq. (II.83).

An important advance for Quantum Chemical applications of TDDFT has been the implementation of analytic derivatives for TDDFT excited states in a number of codes [37,102–107]. This is primarily a matter of calculating $\partial\omega_I/\partial\eta$ to add to $\partial E_0/\partial\eta$ to obtain $\partial E_I/\partial\eta$. It follows from the eigencondition (II.74) that the derivative of the TDA-TDDFT excitation energy is,

$$\partial\omega/\partial\eta = \sum X_{ia}^*(\partial A_{ia,jb}/\partial\eta)X_{jb}. \tag{II.86}$$

This can be further developed as,

$$\frac{\partial\omega}{\partial\eta} = \omega^\eta - \sum_{k,l} M_{kl}S_{kl}^\eta + \sum_{c,k} L_{ck}U_{ck}^\eta, \tag{II.87}$$

where,

$$M_{kl} = \sum_{i,j,a,b} X_{ia}^* X_{jb}\left(\delta_{i,j}K_{ab,kl} - \delta_{a,b}K_{ji,kl} - G_{ia,bj,kl}\right)S_{kl}^\eta$$

$$L_{ck} = \sum_{i,j,a,b} X_{ia}^* X_{jb}\left[\delta_{i,j}\left(K_{ab,kc} + K_{ab,ck}\right)\right.$$
$$\left. - \delta_{a,b}\left(K_{ji,kc} + K_{ji,ck}\right) + \left(G_{ia,jb,ck} + G_{ia,bj,kc}\right)\right]U_{ck}^\eta. \tag{II.88}$$

These are the same as for CIS except for the appearance of the term,

$$G_{pq,p'q',p''q''} = (\partial K_{pq,p'q'}/\partial P_{p''q''}),\qquad\text{(II.89)}$$

which is zero in CIS but involves a triple functional derivative of the xc-functional in TDDFT.

Direct implementation of Eq. (II.87) for calculation of geometric derivatives implies the solution of the coupled perturbed Eq. (II.42) for each geometric degree of freedom. As this would rapidly become prohibitively expensive, it is fortunate that the coupled perturbed coefficients can be replaced by a perturbation-independent Z-vector defined implicitly by,

$$\sum_{c,k} L_{ck} U^{\eta}_{ck} = \sum Z_{ck} \mathscr{B}^0_{ck},\qquad\text{(II.90)}$$

and explicitly by solving the new coupled perturbed equation,

$$\sum_{j,b} \mathscr{A}_{ai,bj} Z_{bj} = L_{ai}.\qquad\text{(II.91)}$$

This is a great saving because this new coupled perturbed equation is independent of the perturbation η and so need only be solved once for each geometry.

One particularly interesting detail which emerges from this discussion is a correction to the RDDM which arises when the excited state MOs are allowed to relax with respect to their values in the ground state. The difference between the reduced density matrix for the Ith excited state and the ground state is given by,

$$\gamma^I_{p,q} - \gamma^0_{p,q} = \frac{\partial \omega_I}{\partial h_{q,p}} = \begin{cases} -\sum_a X^*_{pa} X_{qa}; & p,q \text{ both occupied} \\ +\sum_i X^*_{iq} X_{ip}; & p,q \text{ both unoccupied} , \\ Z_{p,q}; & \text{otherwise} \end{cases}\qquad\text{(II.92)}$$

This allows the calculation of excited-state properties such as true dipole moments, rather than just transition dipole moments, showing that such properties are also accessible from TDDFT. In the past, some programs have made an approximation when calculating excited-state properties by neglecting the Z-vector contribution to the excited-state reduced density matrix.

2.6. Classic problems

It is very important to understand that while LR-TDDFT may be cast into the familiar form of LR-TDHF, the two methods do not behave in the same way. For example, one of the primary problems with LR-TDHF is that HF occupied orbitals see $N-1$ electrons and so are pre-prepared to describe ionization while HF virtual orbitals see N electrons and so are pre-prepared to describe electron attachment. In order to be pre-prepared to describe electronic excitations, the occupied and virtual orbitals should see the same number of electrons which is clearly not the case in HF. In pure DFT, however, both the occupied and virtual orbitals see the same potential and hence the same number of electrons, making DFT a seemingly excellent starting point for describing excitations. Over the years, this positive point has been counter balanced by observations of failures which limit the applicability of conventional (i.e., uncorrected adiabatic) LR-TDDFT. *Clearly it is very important for users to know what these limits are when applying LR-TDDFT. As long as one stays within these limits, TDDFT remains a highly useful tool for many types of applications.*

The first failure to have been pointed out is for Rydberg excitations [34]. More exactly, the ionization potential of a molecule can be considered to be part of its excitation spectrum since electrons excited to high enough energy will be unbound. It can be shown that the ionization continuum in the LR-TDDFT excitation spectrum begins at minus the energy of the highest occupied molecular orbital (HOMO), $-\epsilon_{\text{HOMO}}$. This would not be a problem for the exact xc functional since $-\epsilon_{\text{HOMO}}$ is then the exact ionization potential (I). However the exact xc-functional also possesses a subtle property which is at odds with finding simple analytic forms. This is the particle number derivative discontinuity which tells us that putting even an infinitesimal amount of an electron into the LUMO will provoke a sudden rigid shift of the xc-potential so that the new value of $-\epsilon_{\text{HOMO}}$ will now be the electron affinity (A) of the original system rather than its ionization potential. Typical xc-energy functionals from the lower rungs of Jacob's ladder have xc-potentials whose shape is reasonably good in comparison with that of the exact xc-potential as long as the density is large. However in the outer region, where the density is much smaller, the xc-potentials go much too quickly to zero. As might be expected from continuity arguments,

$$-\epsilon_{\text{HOMO}} \approx \frac{I+A}{2},\qquad\text{(II.93)}$$

for these functionals. This represents an underbinding by as much as about 5 eV (case of N_2). The TDDFT ionization threshold is then too low, leading to a much too early onset of the ionization continuum. Thus high-energy diffuse states, such as Rydberg states, that should be bound fall into an artificially low ionization continuum. The situation is not as grave as might at first be thought because these states persist to some extent as "bound states in the continuum" and can be recovered by using special techniques [108,109]. However trying to describe states that should be bound but which fall into this artificially low ionization continuum remains a difficult task when using conventional finite basis set methods. Hybrid density functionals such as B3LYP help a little with this problem, but not much. A better solution is to include an asymptotic correction to the xc-potential [34,110–113]. Perhaps the most rigorous approach to correcting the asymptotic behavior of the xc-potential is the optimized effective potential (OEP) method which generates the local potential whose orbitals minimize the Hartree-Fock energy expression [114,115]. This approach has been rebaptized the "exact exchange" or EXX method [116,117]. Interestingly Koopmans' theorem works better for the OEP orbital energies than for the original Hartree-Fock energies when compared with experiment [13,118,119]. Even after asymptotic correction, some of the errors in TDDFT calculations are due to errors in Kohn–Sham orbital energies arising from the use of approximate xc-potentials. This is illustrated in the case of ethylene where asymptotic correction of the LDA xc-potential led to an unphysical mixing of the σ- and π-excitation manifolds, an error which was corrected by LR-TDDFT calculations with the LDA xc-kernel and OEP orbitals and orbital energies [13,119].

The second classic problem is the underestimation of charge-transfer excitations. This was already apparent in a dipeptide example treated by Tozer et al. [120] in 1999, but Dreuw, Weisman, and Head-Gordon gave an especially clear explanation of the phenomenon in their paper of 2003 [39]. One way to understand the problem is to go back to our argument about why DFT is pre-prepared to describe electronic excitations involving little or no change in the charge density. This strength of DFT becomes a weakness of DFT when trying to describe excitations involving a transfer of charge from one center to another,

$$A + B \rightarrow A^+ + B^-.\qquad\text{(II.94)}$$

For well-separated systems, A and B, the LR-TDDFT energy for pure density functionals is just an orbital energy difference. However we have already noted that the orbitals are typically underbound. This means that charge transfer excitations are easily underestimated in LR-TDDFT by 1–2 eV. Note however that these problem excitations are perhaps better referred to as "density transfer excitations" since there are many charge transfer excitations in chemistry which

involve little or no density transfer and show no particular problem when described with TDDFT. In fact the classic singlet to singlet charge transfer excitation of Mulliken,

$$H \text{ ---- } H \rightarrow \left[H^+ \, H^- \leftrightarrow H^+ \, H^- \right], \tag{II.95}$$

involves very little change in the charge density. Several approaches for correcting the charge transfer problem in TDDFT have been suggested. Hu, Sugino, and Miyamoto [121,122] have followed up on our work on a charge-transfer correction to TDDFT [97] and the fact that my initial formulation of LR-TDDFT included fractional occupation numbers [5] to incorporate some of the advantages of Slater's transition state approach TDDFT, thereby improving both the description of Rydberg and of charge-transfer excitations. Another approach identifies the problem with the treatment of long-range interelectronic repulsions in DFT. In this approach, the electron repulsion is separated into a short-range part,

$$\left[\frac{1}{r_{12}} \right]_{SR} = \frac{\mathrm{erfc}(\gamma r_{12})}{r_{12}} = \frac{2}{\sqrt{\pi} r_{12}} \int_{r_{12}}^{\infty} e^{-t^2} \, dt, \tag{II.96}$$

which is treated by a purely density-dependent functional and a long range part,

$$\left[\frac{1}{r_{12}} \right]_{LR} = \frac{\mathrm{erf}(\gamma r_{12})}{r_{12}} = \frac{2}{\sqrt{\pi} r_{12}} \int_{0}^{r_{12}} e^{-t^2} \, dt, \tag{II.97}$$

which is described using wave function methods. Here, erf is the usual error function and erfc is the complementary error function.

There are different recipes for choosing the parameter γ and other range separation functions besides the error function are possible. These range-separated hybrids [44,123–126] (other names are also used) yield a significantly better treatment of charge transfer excitations.

A draw-back of the range separated hybrid approach is the existence of a range separation parameter whose value seems to vary with functional and property, though combining the idea of a range separated hybrid with traditional hybrid functionals and reoptimizing the range separation parameter helps in the objective of designing a "universal" functional [127]. In recent work [126,128,129] which appears to be of particular importance for TDDFT, Baer and coworkers have argued that the range separated hybrid parameter γ is not a universal constant but rather should vary depending upon the molecular system and its geometry. They advocate that γ be chosen so that the ΔSCF ionization potential, I, agree as closely as possible with minus the HOMO energy,

$$I(\gamma) = E_N(\gamma) - E_{N-1}(\gamma) \approx -\epsilon_{\mathrm{HOMO}}(\gamma). \tag{II.98}$$

They use this condition to derive a system-dependent optimal value of γ referred to as γ^*. Calculations with their BNL* functional (for Baer-Neuhauser-Livshits with γ^*) show dramatic improvements for both Rydberg and charge-transfer excitations in comparison with results from the range-separated hybrid BNL without system-dependent optimization of γ [128,129].

Very interestingly, a recent EXX study by Gimon et al. shows that errors in the charge transfer excitation of HeH$^+$ are due not to errors in the xc-kernel, but rather to errors in Kohn–Sham orbital energies arising from the use of an approximate xc-potential [130]. A second EXX study by Heßelmann and Görling confirms that a significant part of the error in charge transfer excitation energies is due to errors in the adiabatic TDDFT due to the use of approximate functionals, but goes on to show that an important residual error is due to neglect of the frequency dependence of the xc-kernel [131].

A third problem again arises from the adiabatic approximation. This is the failure of TDDFT to include explicit many-electron excitations. Explicit two-electron excitations are needed to describe the absorption spectra of polyenes where, for example, the first singlet excited state of butadiene, $CH_2{=}CHCH{=}CH_2$, has significant double excitation character [132]. Explicit many-electron excitations are also needed for a proper description of excitations of molecules with open-shell ground states [88]. Exact TDDFT should be able to describe this feature correctly. However the LR-TDDFT Eq. (II.78) has the same dimension as the number of single-electron excitations. When the adiabatic approximation is made, the coupling matrix is frequency independent and the number of solutions of the equation is limited to the number of single-electron excitations, albeit "dressed" to include some correlation effects, in adiabatic LR-TDDFT. Exact TDDFT gets around this problem by allowing the coupling matrix to be frequency dependent. There is then a nonlinear feedback mechanism which allows the matrix equation to have additional solutions. At one point, it was hoped that going beyond linear response to look at, say, *simultaneous* two-photon absorption, would allow two-electron excitations to be treated within the adiabatic approximation [8], however it is now clear that this is not the case. In particular, the poles of the dynamic second hyperpolarizability are identical to the poles of the dynamic polarizability [133], which is to say the one-electron excitations of adiabatic LR-TDDFT. Frequency-dependent xc-kernels which include two-electron excitations explicitly are only beginning to be investigated [42,87–90]. Interestingly two-electron excitations are accessible via *sequential* absorption in real-time TDHF and TDDFT [134].

The fourth and final classic problem to be mentioned here goes by different names in the literature. It contains elements of some of the aforementioned problems, but now the focus is on what happens when a system is made larger and larger. I will refer to the problem as the "scale-up catastrophe." An important goal of DFT is to extrapolate *ab initio* accuracy to molecules too large to otherwise treat by conventional (i.e., HF-based) *ab initio* calculations. The usual recommendation is to test DFT calculations on small molecules where comparisons can be made with accurate *ab initio* calculations and then to *assume* that DFT calculations which are reliable for a given class of molecule and molecular properties will remain accurate as the size of the molecules treated is increased (i.e., scaled-up). When instead inaccuracies increase as the size of the system is increased, then we have a scale-up catastrophe. One example of a scale-up catastrophe in LR-TDDFT occurs in periodic systems where the xc-kernel vanishes on the lower rungs of Jacob's ladder due to improper scaling with respect to the number of K points [135]. The result is that the first vertical excitation energy reduces to just the difference between the HOMO and LUMO orbital energies, which is too low. However this is often not a disaster because little or no oscillator strength is associated with this transition. Instead the general shape of the optical absorption spectra often remains reasonable since post-DFT time-dependent Hartree theory (TDH/DFT) is often (though not always) a good approximation. A more disturbing example of a scale-up catastrophe is that studies on oligomers of conducting polymers showed that dynamic polarizabilities could be overestimated by arbitrarily large amounts by simply going to a large enough oligomer [35,136]. There are several phenomena which can be invoked to help to understand this phenomenon. For example, we have already seen how TDDFT underestimates charge transfer excitation energies, meaning that charge is transferred too easily from one part of the molecule to another. Naïvely, our molecule is acting too much like the homogeneous electron gas, a conductor which is the basis of almost all density functionals, and it is well known that electric fields applied to perfect conductors lead to the build up of surface charges which cancel the applied fields in the interior of the conductor (Faraday effect). A solid-state physicist would say that the band gap is being underestimated, and that this could be due to problems in calculating the Kohn–Sham orbital energies or due to the failure to include derivative discontinuities in the

xc-potential. But the reaction field which cancels the applied field in the interior of the conductor is given by the response of the self-consistent field which depends on the description of the xc-kernel. This xc-kernel must be "ultra-nonlocal" in the sense that it must react to charges built up on the surface of the conductor. On the lower rungs of Jacob's ladder,

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2) \approx f_{xc}(\mathbf{r}_1, \mathbf{r}_2)\delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{II.99}$$

whereas a rough estimate of the exchange-only part of the xc-kernel [93] suggests that it should go more like,

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2) \cong -\frac{|\gamma(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)r_{12}\rho(\mathbf{r}_2)}. \tag{II.100}$$

In fact, for systems containing only two electrons this becomes the exact exchange-only result [137],

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{r_{12}}. \tag{II.101}$$

Thus a diagonal xc-kernel [Eq. (II.99)] is certainly incorrect. Let us take a moment to absorb this: Walter Kohn has emphasized the short-sighted nature of the xc-potential and this is basically true. However the xc-kernel, which is just the functional derivative of the xc-potential, need not be—and is not—short-sighted, meaning that the xc-potential itself contains a response component which is not short-sighted [138]. There are few choices for dealing with this problem—either one restricts oneself to medium-sized systems before the onset of the scale-up catastrophe or one climbs Jacob's ladder to use more sophisticated functionals. One way to restrict oneself to medium-sized systems is to use a subsystem theory such as Kohn–Sham equations with constrained density (KSECD) which allows us to perform LR-TDDFT calculations to obtain localized excitations for a medium-sized subsystem of a much larger system, such as for a solvated molecule [43,139,140]. Climbing Jacob's ladder to functionals with contributions from Hartree-Fock exchange is also helpful as is the use of range-separated hybrids [44,123–125]. Another approach which is helpful in some cases is time-dependent current-density functional with the Vignale–Kohn functional [141,142]. This is because the current can carry information about perturbations at a distance. A very recent approach to the scale-up catastrophe, is to use an xc-kernel derived from the Bethe–Salpeter equation. This has been used to improve the description of excitons [143,144], including in the excitation spectra of polyacetylene and chains of H_2 [145].

Having made a list of some of the most important failures of conventional TDDFT, let us summarize by saying that LR-TDDFT has been found to work best for (i) low-energy (ii) one-electron excitations involving (iii) little or no charge transfer and (iv) which are not too delocalized.

3. Modern evolutions

The present volume illustrates some of the current trends in the use and development of TDDFT for molecules and molecular solids, by leading researchers in this field.

3.1. Functionals and corrections

As high-lighted in the previous section, TDDFT places new demands on xc-functionals. It does this primarily by looking at properties which are not normally treated with conventional static ground-state DFT, but may include aspects of the time-dependent xc-functional which are intrinsically absent in the xc-energy functional. For this reason the testing of functionals and proposals for correcting functionals is very important. This aspect is clearly seen in Perpète and Jacquemin's work on benchmarking TDDFT for indi-

goïd dyes in the present volume [146]. An important question addressed is the amount of Hartree-Fock exchange which needs to be included in the xc-functional.

One approach to improving functionals begins with the observation that excitation energies obtained with LR-TDDFT and the ΔSCF multiplet sum method (MSM) basically agree when both methods are expected to apply [5,97,122,147]. It is well-known that LR-TDHF TDA calculations and the ΔSCF Hartree-Fock MSM give identical formulae in the two-orbital model. However the same thing does not quite happen for TDDFT and ΔSCF MSM DFT [5]. Understanding why could be a way to improve either or both TDDFT and ΔSCF MSM DFT and I am happy to see continuing active work on this problem [148]. Historically Casida et al. were apparently the first to try to use analogies between TDDFT and ΔSCF MSM DFT to introduce a correction to LR-TDDFT calculations for charge transfer effects [97,149]. Hu, Sugino, and Miyamoto have followed up this work to develop their own approach to correcting problems with underestimated Rydberg and charge transfer excitations [121,122]. In this volume, Ziegler et al. take a similar but different approach in which they include an infinite order resummation of higher-order response theory terms which give ΔSCF-like diagonal terms in the LR-TDDFT matrix eigenvalue problem [150].

Both Ipatov, Cordova, Joubert Doriol, and Casida [101] and Rinkevicius, Vahtras, and Ågren [94] mention the importance of going beyond the TDDFT adiabatic approximation for handling excitation spectra of molecules with an open-shell ground-state. Baer [55] discusses when it is and is not necessary to go beyond the adiabatic approximation in TDDFT.

Previous work in developing functionals has benefited from the development of benchmark test sets. It is far too easy to underestimate the work involved in developing good benchmark sets. The initial work on TDDFT encountered the difficulty that very few molecules had well characterized excited states. It is thus good to see recent efforts testing TDDFT for a wide variety of compounds [151,152]. It is especially encouraging to see the development of expanded benchmark data bases for excited states based upon both experimental data and high-quality *ab initio* calculations [52,53]. It is hoped that these benchmark sets will further aid researchers in their quest to improve functionals for TDDFT. Expansion of these benchmark sets to include inorganic compounds and potential energy surfaces is highly desirable.

3.2. Diagnostic tools

One of the characteristics of modern *ab initio* methods is that some of them include diagnostic tools which warn the user when the method is no longer applicable. Such tools are also very much needed in TDDFT to see when the xc-functional is inadequate. This volume contains two examples of such tools.

The first example concerns excitations of molecules with an open-shell ground state. Because conventional TDDFT cannot flip spins, it is limited to singlet- and triplet-coupled excitation operators. For a molecule with a closed-shell ground state, this is no problem since singlet-coupled excitations of a singlet are singlets and triplet-coupled excitations of a singlet are triplets. However problems arise for molecules with open-shell ground-states because typically only the singlet-coupled excitations will yield spin-eigenfunctions. Moreover the spin-coupling of the excitation operators is not perfectly clear in a spin-unrestricted formalism where different orbitals are used for different spin. In the present volume, Ipatov, Cordova, Joubert Doriol, and Casida discuss the calculation of spin-contamination for TDDFT excited states and show how to separate unphysical artifacts from potentially meaningful excited states [101].

The second example concerns charge-transfer excitations, which I have emphasized are perhaps better described as density-transfer excitations. In their contribution, Peach and Tozer follow up on earlier work [153] showing how excitations can be analyzed for density-transfer character [154]. They obtain a quantitative correlation between underestimations of excitation energies by TDDFT and their measure of charge-transfer.

3.3. More realistic spectra

Important advances have been made in including more physics in calculated spectra, including vibrational effects and solvent effects.

If we concentrate on carefully-done low-pressure gas phase experiments, then the main effect is believed to be vibrational broadening, due to the superposition of a number of Franck-Condon transitions. Elementary theory suggests that the most probable transition (peak in the absorption spectrum) corresponds roughly to the vertical excitation energy from the equilibrium geometry of the ground state. However this estimate of vertical excitation energies typically contains errors of up to about 0.2 eV. (Incidently this is one reason that it was difficult in the past to claim a theoretical model for calculating vertical excitations to be better than about this accuracy.) Moreover the vibrational envelopes of the vertical transitions are broad and overlapping. It is thus important to include vibronic effects when simulating spectra, something which has only become possible by the ability to calculate analytic derivatives for the ground- and excited-states [37,102–107]. The basic procedure has been worked out and implemented by Dierksen and Grimme with excellent results [45]. Later, Santoro et al. [155–157] implemented their approach to the same problem in the code FCLASSES [158]. The essential idea is to treat the ground- and excited-state potential energy surfaces are harmonic and shifted one with respect to the other, and then to calculate the Franck-Condon transitions for these *N*-dimensional harmonic oscillators. This program has been used to include vibrational structure in the studies of De Angelis and Fantacci [159] and Peltier et al. [160] in this volume.

Solvent shifts on absorption spectra are also known to be large. To my knowledge the first inclusion of solvent effects in TDDFT spectra is that of Cossi and Barone using the polarizable continuum model (PCM) [161]. Their approach assumes the two-component Pekar model. This model is separated by time scales into a fast and slow part. The slow part represents molecular orientations which do not have time to readjust during excitations while the fast part represents solvent electronic degrees of liberty which do have time to adjust during the excitation. This fast part must be included in the reaction field of the PCM and so enters into the LR-TDDFT equations. This model of the solvent shift has been used by De Angelis and Fantacci [159], by Perpète and Jacquemin [146], and by Peltier et al. [160] in this volume.

3.4. New systems/properties

Over the years, TDDFT has been extended to treat an increasingly larger number of systems and properties. Among the several notable efforts in this regard has been the development of the "toolbox" approach by Ågren and coworkers [162] which is used in both the articles of Rinkevicius, Vahtras, and Ågren [94] and of De Angelis and Fantacci [159] in this volume. A new type of system discussed here consists of molecules with open-shell groundstates. New properties include spin-orbit coupling and phase-space properties.

The problem of extending TDDFT to open-shell molecules is explicitly treated by Ipatov, Cordova, Joubert Doriol, and Casida [101] and by Rinkevicius, Vahtras, and Ågren [94]. The two ap-

proaches are different in that Ipatov, Cordova, Joubert Doriol, and Casida focus on spin-unrestricted (different-orbitals-for-different-spin) calculations while Rinkevicius, Vahtras, and Ågren focus on restricted open-shell Kohn–Sham (same-orbitals-for-different-spin) calculations, but are evidently interrelated. In fact, Rinkevicius, Telyatnyk, Vahtras and Ågren made the connection in their restricted–unrestricted approach to calculating hyperfine coupling constants where they use a spin-restricted formulation to simulate the effect of spin polarization on property calculations [163–165].

In this volume, Ipatov, Cordova, Joubert Doriol, and Casida limit themselves to discussing the calculation of spin contamination. (A more general discussion of open-shell problems in TDDFT was given in Ref. [98].) In contrast Rinkevicius, Vahtras, and Ågren have introduced explicitly spin-coupled excitation operators to handle open-shell molecules [94]. (See Refs. [166,167] for closely related work.) Both Ipatov, Cordova, Joubert Doriol, and Casida and Rinkevicius, Vahtras, and Ågren point out the need to be able to handle two- and higher-electron excitations explicitly in order to have a complete treatment of excitations in open-shell molecules.

De Angelis and Fantucci include spin-orbit coupling in their TDDFT calculations [159] using the quadratic response theory formulation of TDDFT developed in the Ågren group [162] and the two-component relativistic zero-order regular approximation (ZORA) solution of the LR-TDDFT equations from the Ziegler group [47,48].

Both conventional DFT and conventional TDDFT are restricted to describing the response of the charge density, as opposed to the momentum density. In the present volume, Rajam, Hessler, Gaun, and Maitra consider the advantages and difficulties of extending TDDFT into phase space [72].

3.5. Photochemistry

In this author's opinion, one of the next great frontiers after spectroscopy is certainly photochemistry. While spectroscopy focuses on electronic processes involving relatively small changes in molecular geometries, photochemical modeling tries to predict the complex pathway of an entire photochemical reaction. TDDFT is already used to describe initial excited states in photochemistry and the beginning of reaction paths [168–171], but could it be used to follow a reaction from start to finish? The most natural first approach is to use a semiclassical approach in which the electrons are described quantum mechanically and the nuclei are described classically. These approaches have been conveniently reviewed in the context of DFT by Doltsinis and Marx [172] and divide into two main approaches.

The earliest attempts to use TDDFT to describe photochemistry make use of the Ehrenfest (also called the eikonal or mean-field) approximation. In the most general formulation of this semiclassical method, the electrons move quantum mechanically in the time-dependent field of the moving nuclei,

$$\widehat{H}_{\text{elec}}(\mathbf{R}(t))\Psi(\mathbf{r},t) = i\frac{\partial}{\partial t}\Psi(\mathbf{r},t), \tag{III.1}$$

and the nuclei move classically according to forces calculated from expectation values of potential energies,

$$V_{\text{nucl}}(\mathbf{R}(t)) = \langle \Psi(t) \mid \widehat{H}_{\text{elec}}(\mathbf{R}(t)) \mid \Psi(t) \rangle + \sum_{IJ}\frac{Z_I Z_J}{R_{IJ}(t)}. \tag{III.2}$$

In the context of TDDFT, the quantum mechanical equation to solve for the electrons is the TDDFT equation in real-time. This approach has been used to study the photo- and collision-induced dynamics of alkali metal clusters [173–177] and of small molecules [178]. The calculation is deterministic in the sense that the nuclei move on a single, time-averaged, Born–Oppenheimer surface. Unfortunately

this prevents to some extent the calculation of product branching ratios (relative yields) of photochemical reactions which arise from the presence of multiple potential energy surfaces and finite probabilities for jumping from one to the other. (Other problems are mentionned in the article of Doltsinis and Marx [172].)

An in principle more rigorous (though still not completely rigorous, because semiclassical) approach is Tully's surface hopping model [179,180]. Eq. (III.1) is solved as a linear combination of the Born–Oppenheimer wave functions,

$$\Psi(\mathbf{r}, t) = \sum_I \Psi_I(\mathbf{r}; \mathbf{R}(t)) C_I(t), \qquad (III.3)$$

The square of the coefficient $|C_I(t)|^2$ gives the probability of finding a trajectory on the Ith potential energy surface. Additional tricks are needed to make the algorithm practical, but this is the basic idea. In addition to branching ratios which arise from different initial conditions (something taken into account in Ehrenfest dynamics), additional branching contributions now arise due to surface hopping. The first fairly rigorous implementation of mixed TDDFT/classical trajectory surface hopping was made by Tapavicza, Tavernelli, and Rothlisberger in the program CPMD [50], followed by a very nice application to oxirane photodynamics [100]. The fact that a similar implementation has been made by Bonačić-Koutecký and coworkers in the program TURBOMOL [181,182], means that we are likely to see many more applications of this TDDFT approach to photodynamics in the near future. The article by Niehaus in the present volume also discusses photodynamic modeling via the time-dependent density-functional tight-binding method (TD-DFTB) [183].

Nevertheless two major issues have tended to plague this type of application. The first issue is the question of whether nonadiabatic coupling matrix elements can in principle be calculated in TDDFT and to what accuracy they can be calculated in practice. Nonadiabatic coupling matrix elements directly influence surface hopping probabilities. This topic was explicitly reviewed in Appendix A of Ref. [99] where it was pointed out that, in principle, linear response theory allows the explicit calculation of nonadiabatic coupling matrix elements in TDDFT between the ground and excited states, and previous assessments of the quality of TDDFT nonadiabatic coupling matrix elements were reviewed. (See also Ref. [184].) In the present volume, Tavernelli, Tapavicza, and Rothlisberger assess their algorithm for calculation for calculating nonadiabatic coupling matrix elements in TDDFT [185]. In principle, calculations of nonadiabatic coupling matrix elements between two excited states should also be possible via quadratic response theory [94], but the method will need to be carefully validated for different types of excitations.

The second major issue plaguing the application of TDDFT to photochemistry is the question of the existence of conical intersections (CXs) between the DFT groundstate and TDDFT excited states. At the risk of oversimplification, once a photon excites a molecule to an electronically excited state, the molecule has only a very short window of time in which it can perform photochemistry before competing processes return it to its groundstate. One of the best ways to pass quickly (i.e., within the space of about one vibration) from an excited state to product groundstates is to pass through CXs, hence the great importance often assigned to these states in post-1990s photochemical modeling. However Levine, Ko, Quenneville, and Martinez successfully argued in their article of 2006 that exact CXs cannot exist between ground and excited states in adiabatic TDDFT [186]. While this certainly has implications for quantitative applications of mixed TDDFT/classical trajectory surface hopping, the study of Tapavicza et al. is certainly comforting in that it shows that TDDFT is able to provide an approximate description of a CX as interpenetrating double cones [100].

It will indeed be highly interesting to see how this type of application, which has only recently come on-line within the last 3 years, evolves over the years to come.

3.6. Multiscale modeling

The preface to this volume explicity mentions the timeliness of TDDFT for studying nanosystems. Such applications are nicely illustrated by the article of Vasiliev et al. in this volume reporting their application of their real-space program PARSEC to carbon nanotubes, organic light-emitting diodes (OLEDs), and silicon clusters [187]. (Kawashita et al. report calculations on C_{60} [188] and De Angelis and Fantucci also discuss light-emitting devices [159].) The efficiency of PARSEC allows TDDFT calculations over a wide range of molecular sizes.

Size effects over logarithmic size scales is certainly a hallmark of present-day modeling of nanosystems. No one method—not even TDDFT—is capable of spanning the full range of scales of interest. Instead modern modeling of nanosystems emphasizes multiscale modeling where different techniques are used for different size ranges, but parameters from one size range can be obtained by direct comparison with the results of other methods in adjacent overlapping size ranges. In this volume, Niehaus describes one such method, namely time-dependent density-functional tightbinding (TD-DFTB), which takes its parameters directly from TDDFT calculations but provides an order-N method for studies on larger molecules than could otherwise be handled by ordinary TDDFT [183].

3.7. Beyond linear response

One of the important advantages of a fully time-dependent method is the ability to go beyond linear response theory. In their article in this volume, after presenting an alternative derivation of Casida's equation, Rinkevicius, Vahtras, and Ågren develop quadratic response theory for TDDFT [94]. While quadratic response calculations in TDDFT go back to as early as 1991 [189–191], the work in the Ågren group is particularly well adapted to applications in quantum chemistry. In particular, it opens up the very exciting possibility of calculating transition matrix elements between two excited states as well as permitting the calculation of properties of a single excited state.

Quadratic response theory still depends upon the perturbed system being initially in the ground stationary state. Real-time TDDFT not only opens the possibility to go to infinite order in response theory, but also means that the perturbed system can be taken well beyond the initial ground stationary state [192]. Indeed the simplicity of TDDFT calculations makes it difficult for other methods to compete in this type of application. Also, as Kawashita et al. so nicely illustrate in this volume, real-time TDDFT is also a very effective way to extend the spectral range of linear response calculations beyond what is normally accessible using usual Quantum Chemistry techniques [188]. Nevertheless real-time TDDFT calculations are not without formal and practical problems. One of these is the need to go beyond the TDDFT adiabatic approximation to include memory effects [78–81]. In this volume, Baer points out that the adiabatic approximation applies not only to weak low-frequency perturbations, but also to intense very-high frequency perturbations [55]. Thus the adiabatic approximation applies at both extremes and memory effects only become a problem in-between. In their article in this volume, Rajam, Hessler, Gaun, and Maitra remind us that formally exact real-time TDDFT depends not only on the charge density but also on the initial *wave function* which can only be replaced by the charge density when the system is initially in the ground stationary state [72].

4. Perspectives

It has been nearly 3 decades since the first pragmatic application of TDDFT [3] and about 2 1/2 decades since the Runge–Gross theorem [4] laid a firm formal foundation for TDDFT. During this time, TDDFT has become the main single-determinantal approach to treating the excited states of medium-sized and large molecules, partly because of technical advances such as a time-dependent Hartree-Fock-like formulation of LR-TDDFT [5], analytic derivatives for excited states [37], quadratic response theory, [40], incorporation of solvent effects [38] and vibrational effects [155], and now Tully-like photodynamics [50]. These have really helped to open up large parts of Physical Chemistry and Chemical Physics to TDDFT modeling. There is no reason to expect these technical advances to slow down and indeed the whole area of TDDFT-based photodynamics seems poised to open up new frontiers.

At the same time, many problems have been established with conventional LR-TDDFT. Rydberg [34] and charge-transfer [39] are badly underestimated; there is also a need for explicit inclusion of two- and higher-electron excitations [42]; and there is even a scale-up catastrophe, particularly for conducting polymers [35]. This still leaves lots of applications where TDDFT is an appropriate method of choice. For other applications, difficulties can be overcome just by fine tuning existant functionals (often by varying the amount of Hartree-Fock exchange). Still other applications require a more drastic procedures, including but not limited to exact exchange [33], KSCED subsystem theory [43], or range-separated hybrids [44]. Going beyond the TDDFT adiabatic approximation to include frequency dependence in the xc-kernel seems urgent. Fundamental studies are certainly welcome as relatively little is known about the frequency dependence of the exact $f_{xc}(\omega)$.

Perhaps it is worth recalling that it has been about 4 1/2 decades since the seminal papers of Hohenberg, Kohn, and Sham [1,2]. The present use of the adiabatic approximation in TDDFT reminds me a bit of the state of DFT in the early 1980s when little was available beyond the LDA. The Perdew–Zunger self-interaction correction seemed a major step forward [193]. But little did we suspect the explosion of activity that would be opened up by generalized gradient approximations (GGAs) [194,195]. Is something comparable waiting for TDDFT just around the corner?

My feeling is that the present work on memory effects, phase-space and density-matrix functional theory, optimized effective potential methods, open-shell systems, spin-flip, and fractional occupation number provide important but still too much orthogonal advances. I am thinking that it is about time for another fundamental advance, perhaps unifying many of the above approaches.

In the meantime, there is an aspect of TDDFT which has not yet been touched upon in this brief, biased, review article, disguised as an introduction. DFT has almost completely replaced Hartree-Fock in quantum chemistry *except* as a starting point for post-Hartree-Fock many-body theories. *What about post-DFT many-body theories?* It may come as a surprise to some readers that post-DFT many-body theories are the norm, rather than the exception, in solid-state physics, where *GW* and Bethe–Salpeter calculations invariably start by solving the Kohn–Sham equation [86]. Not only is this one pragmatic way to correct conventional DFT, but it can also provide insights into the behavior of exact xc-potentials and kernels. And there are potentially important real computational advantages to be gained by using DFT and TDDFT functionals to re-sum many-body diagrams. Why redo all that many-body theory for yet another system if we can already take advantage of functionals obtained by doing many-body theory on the perturbed homogeneous electron gas? Indeed this is also an active direction and perhaps it, together with lots of trial and error and some fundamental physical insight, will be the source of the next fundamental advance.

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