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Density functional methods for excited states: equilibrium structure and electronic spectra

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1. INTRODUCTION

Density functional theory (DFT) is nowadays one of the most popular methods for ground state electronic structure calculations in quantum chemistry and solid state physics. Compared to traditional *ab initio* and semi-empirical approaches, contemporary density functional methods show a favorable balance between accuracy and computational efficiency. A number of commercial programs is available, and DFT calculations of ground state energies, structures, and many other properties are routinely performed by non-experts in (bio-)chemistry, physics, and materials sciences.

Hohenberg-Kohn density functional theory is strictly limited to ground states [1], which excludes applications to photochemistry. This is a serious drawback, because photoexcited molecules are experimentally much more difficult to characterize than molecules in their ground states. Reliable theoretical predictions for excited states are thus especially valuable.

Several routes have been followed to extend conventional DFT to excited states (see, e.g., Refs. [2–5]). In the present review, we focus on time-dependent density functional theory (TDDFT), which is presently the most popular method to treat excited states in a DFT framework. Extensive reviews on TDDFT exist [6–10]; most of them emphasize formal aspects of the theory. The aim of the present work is to survey the use of TDDFT in photochemistry. It is primarily written for non-experts with little background in DFT. The literature in this field is growing rapidly, and we cannot claim to be exhaustive; instead, we give a selective introduction to important concepts and recent developments from a rather personal perspective.

Sec. 2 contains a brief introduction to the theory. We do not give any derivations and merely state the most important results and explain their meaning. An overview of popular density functionals is given in Sec. 2.3. Algorithms to compute spectra and excited state properties are reviewed in Sec. 3. We mostly describe the steps necessary in a TDDFT excited state calculation and give details only where necessary. Some timings for typical applications are presented in Sec. 3.4. Sec. 4 summarizes the performance of TDDFT excitation energies, transition moments, and excited state properties

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in benchmark studies. This section is recommended to the reader interested in the accuracy of TDDFT in general. Situations where present functionals fail are discussed as well. Specific applications are surveyed in Sec. 5. Classes of compounds include aromatic systems and fullerenes, porphyrins and related compounds, transition metal compounds, metal and semiconductor clusters, organic polymers, and biologically relevant systems. We close with an outlook in Sec. 6.

2. THEORETICAL FOUNDATIONS

2.1. Time-dependent response theory approach to excited states

Excited states are solutions of the *time-independent* stationary Schrödinger equation; time-dependent response theory is used as a trick to reduce electronic excitations to ground state properties. Consider a molecule in its electronic ground state subject to a periodic perturbation by a uniform electric field \mathbf{E} oscillating at frequency ω . The distribution of the electronic charge and current density of the molecule is described by the one-particle density matrix $\gamma(t)$. $\gamma(t)$ will perform driven oscillations about its ground state value $\gamma^{(0)}$. The amplitude of these oscillations is given by the Fourier transform of $\gamma(t)$, denoted $\gamma(\omega)$ for simplicity. As a result of elementary perturbation theory, $\gamma(\omega)$ has the following expansion in powers of the field \mathbf{E} :

$$\gamma(\omega) = \gamma^{(0)} - \sum_n \left(\frac{\gamma_{0n} \boldsymbol{\mu}_{0n}}{\omega - \Omega_{0n}} - \frac{\gamma_{0n}^\dagger \boldsymbol{\mu}_{0n}^*}{\omega + \Omega_{0n}} \right) \mathbf{E} + O(E^2) \quad (1)$$

If the frequency ω approaches an excitation energy Ω_{0n} of the system, there is a *resonance catastrophe* and the amplitude of the oscillation diverges. Keeping the analogy to a system of harmonic oscillators [11, 12], the excitation energies Ω_{0n} are the *eigenfrequencies* of the electrons in the molecule, and the transition density matrices γ_{0n} are the corresponding *collective* modes. After inversion of the relation between $\gamma(\omega)$ and \mathbf{E} , the excitation energies are obtained as eigenvalues of an *electronic Hessian* which may be imagined as the matrix of second derivatives of the electron energy with respect to the electronic degrees of freedom.

In this way, any ground-state theory can be extended to excited states, provided the time-dependent response is well-defined. The thus obtained excitation energies and transition moments are in turn consistent with ground-state properties because sum over states (SOS) expressions as in Eq. (1) hold. Both is generally not true for state-based methods. On the other hand, the reliability of response theory based methods crucially depends on the stability of the ground state (see below).

The formal basis for an extension of common ground-state density functional methods to time-dependent perturbations is TDDFT. Within the time-dependent Kohn-Sham (TDKS) framework [13], one considers a system of N non-interacting fermions whose density is constrained to the physical density $\rho(t, x)$. This leads to the time-dependent Kohn-Sham equations

$$i \frac{\partial}{\partial t} \phi_j(t, x) = H[\rho](t, x) \phi_j(t, x). \quad (2)$$

The effective TDKS one-particle Hamiltonian $H[\rho](t, x) = \pi^2(t, x)/2 + v_s[\rho](t, x)$ consists of a kinetic energy part and a local time-dependent external potential $v_s[\rho]$. The latter is

a unique functional of $\rho(t, x)$ (up to a gauge transformation) for a given initial state, as stated by Runge and Gross [13]. v_s is usually decomposed according to

$$v_s[\rho](t, x) = v_{\text{ext}}(t, x) + v_C[\rho](t, x) + v_{\text{xc}}[\rho](t, x) \quad (3)$$

into the external one-particle potential v_{ext} , the time-dependent Coulomb (or Hartree) potential $v_C[\rho](t, x) = \int dx' \rho(t, x')/|\mathbf{r} - \mathbf{r}'|$, and the time-dependent exchange-correlation potential $v_{\text{xc}}[\rho](t, x)$.

Equivalently, one may consider the TDKS one-particle density matrix $\gamma(t)$, which is related to the TDKS orbitals via the spectral representation

$$\gamma(t, x, x') = \sum_{j=1}^N \phi_j(t, x) \phi_j^*(t, x'). \quad (4)$$

Its time evolution is governed by the von-Neumann equation

$$i \frac{\partial}{\partial t} \gamma(t) = [H[\rho](t), \gamma(t)], \quad (5)$$

subject to the idempotency constraint

$$\gamma(t, x, x') = \int dx_1 \gamma(t, x, x_1) \gamma(t, x_1, x'). \quad (6)$$

This *density matrix based approach* [12, 14–16] is particularly convenient for response theory, because the equations determining the first and higher order response of γ can be derived by straightforward differentiation of Eqs. (5) and (6) with respect to an external perturbation [15]. Complicated intermediates such as perturbed orbitals or response functions are avoided.

Equations (5) and (6) describe a non-interacting system and are therefore computationally manageable, while the solution of the full interacting N -electron problem is exponentially more complex. This is, somewhat simplified, the main cause of the computational advantage of density functional methods over conventional wave-function methods. The price for this improved efficiency is that the potential $v_{\text{xc}}[\rho](t, x)$ has to be approximated. The construction of accurate and inexpensive approximations to $v_{\text{xc}}[\rho]$ is a central problem of TDDFT and will be discussed in Sec. 2.3. Formally, the TDKS construction implies [6] that $\gamma(t)$ yields the *interacting* density ρ and the *interacting* current density \mathbf{j} according to

$$\begin{aligned} \rho(t, x) &= \gamma(t, x, x) \\ \mathbf{j}(t, x) &= \frac{1}{2} (\boldsymbol{\pi}(t, x) + \boldsymbol{\pi}^*(t, x')) \gamma(t, x, x') \Big|_{x'=x}. \end{aligned} \quad (7)$$

This means that the frequency-dependent TDKS density matrix response must have an SOS expansion of the type (1). Therefore, the *physical* excitation energies are accessible from the TDKS response, and the corresponding eigenmodes yield *physical* transition moments.

2.2. Excited state properties

2.2.1. The Lagrangian of the excitation energy

The time-dependent response theory approach outlined in the last section provides a route to excitation energies and transition moments. Excited state total energies are accessible by adding the corresponding ground state energy to the excitation energy. But how to compute other excited state properties such as dipole moments *without* an excited state wavefunction? – First it is important to remember that the wavefunction is only an intermediate that relates properties of a system such as energies or densities to a Hamiltonian, i.e., external potentials. Properties of a stationary state may be defined without reference to the wavefunction by the dependence of the energy on an applied external perturbation. For example, the dipole moment may be defined as the first derivative of the energy with respect to a constant electric field at zero field strength. More generally, the excited state density can be defined as the functional derivative of the excited state energy with respect to an external perturbing potential at zero coupling. It is therefore sufficient to know the *dependence of the excited state energy on the external potential* to compute static excited state properties.

The energy of a stationary state is stable with respect to the wavefunction; this leads to the Hellmann-Feynman theorem for first-order properties and to the more general Wigner $2n + 1$ rule. The latter states that the wavefunction through n -th order determines all properties through order $2n + 1$. The Lagrangian method establishes an analogous variational principle for excited states in TDDFT. Here we present a summary only; for a detailed derivation, the reader is referred to Ref. [17].

The Lagrangian of the excitation energy is defined by

$$L[X, Y, \Omega, C, Z, W] = \langle X, Y | \Lambda | X, Y \rangle - \Omega (\langle X, Y | \Delta | X, Y \rangle - 1) + \sum_{ia\sigma} Z_{ia\sigma} F_{ia\sigma} - \sum_{pq\sigma} W_{pq\sigma} (S_{pq\sigma} - \delta_{pq}). \quad (8)$$

F is the ground state Fock matrix, and S denotes the overlap matrix. L depends on the ground state Kohn-Sham (KS) molecular orbital (MO) coefficients C ; the latter are related to the ground state KS MOs $\phi_{p\sigma}$ via the LCAO (linear combination of atomic orbitals)

$$\phi_{p\sigma}(\mathbf{r}) = \sum_{\nu} C_{\nu p\sigma} \chi_{\nu}(\mathbf{r}), \quad (9)$$

where χ_{ν} are atom-centered basis functions. Indices i, j, \dots are used for occupied, a, b, \dots for virtual, and p, q, \dots for general MOs. We assume that the MOs are real and eigenfunctions of the z component of the total spin. X and Y parameterize the transition density matrix γ_{0n} of the n -th excited state,

$$\gamma_{0n\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{ia} (X_{nia\sigma} \phi_{a\sigma}(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}') + Y_{nia\sigma} \phi_{i\sigma}(\mathbf{r}) \phi_{a\sigma}(\mathbf{r}')); \quad (10)$$

we shall always refer to the n -th state and omit state labels where possible. X and Y are conveniently gathered in the two component “transition vector”

$$\begin{pmatrix} X \\ Y \end{pmatrix} = |X, Y\rangle. \quad (11)$$

Ω , Z , and W are Lagrange multipliers enforcing additional constraints, as discussed below. If L becomes stationary, the additional “penalty” terms introduced by Ω , Z , and W vanish by construction. One is thus left with the term $\langle X, Y | \Lambda | X, Y \rangle$ representing the excitation energy. It may be considered an expectation value of the orbital rotation Hessian Λ evaluated for the transition vector $|X, Y\rangle$. Λ and Δ are 2×2 “super-operators”,

$$\Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (12)$$

where A and B have the matrix representation

$$(A + B)_{ia\sigma jb\sigma'} = (\epsilon_{a\sigma} - \epsilon_{i\sigma})\delta_{ij}\delta_{ab}\delta_{\sigma\sigma'} + 2(ia\sigma|jb\sigma') + 2f_{ia\sigma jb\sigma'}^{\text{xc}} - c_x\delta_{\sigma\sigma'}[(ja\sigma|ib\sigma) + (ab\sigma|ij\sigma)] \quad (13a)$$

$$(A - B)_{ia\sigma jb\sigma'} = (\epsilon_{a\sigma} - \epsilon_{i\sigma})\delta_{ij}\delta_{ab}\delta_{\sigma\sigma'} + c_x\delta_{\sigma\sigma'}[(ja\sigma|ib\sigma) - (ab\sigma|ij\sigma)]. \quad (13b)$$

$(pq\sigma|rs\sigma')$ is a two-electron repulsion integral in Mulliken notation, and $f_{pq\sigma rs\sigma'}^{\text{xc}}$ represents a matrix element of the exchange-correlation kernel in the adiabatic approximation (AA),

$$f_{\sigma\sigma'}^{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E^{\text{xc}}}{\delta\rho_\sigma(\mathbf{r})\delta\rho_{\sigma'}(\mathbf{r}')}, \quad (14)$$

where E^{xc} is the *static* exchange-correlation energy functional. The hybrid mixing parameter c_x [18, 19] is used to interpolate between the limits of “pure” density functionals ($c_x = 0$) and time-dependent Hartree-Fock (TDHF) theory ($c_x = 1$, $E^{\text{xc}} = 0$).

2.2.2. Stationarity conditions for L

The following stationarity conditions determine the excited state energy and first order properties.

1. The ground-state KS equations (in unitary invariant form),

$$\frac{\delta L}{\delta Z_{ia\sigma}} = F_{ia\sigma} = 0, \quad (15)$$

implying that the occupied-virtual block of the ground-state Fock operator F is zero. The Lagrange multiplier W enforces orthonormality of the KS MOs,

$$\frac{\delta L}{\delta W_{pq\sigma}} = S_{pq\sigma} - \delta_{pq} = 0. \quad (16)$$

2. The TDKS eigenvalue problem (EVP)

$$\frac{\delta L}{\delta \langle X, Y |} = (\Lambda - \Omega\Delta)|X, Y\rangle = 0, \quad (17)$$

together with the non-standard normalization condition for the transition vectors

$$\frac{\delta L}{\delta \Omega} = \langle X, Y | \Delta | X, Y \rangle - 1 = 0, \quad (18)$$

which is enforced by Ω . The form of Eqs. (17) and (18) is familiar from Hartree-Fock (HF) theory [20]. This analogy was first recognized by Zangwil and Soven [21] and later

generalized by Casida [14]. Other schemes, including density based methods [22] and Dyson-type procedures [23] are special cases of the density matrix based formalism.

The eigenvalues Ω of Λ are electronic excitation energies, and the corresponding transition vectors $|X, Y\rangle$ are collective eigenmodes of the TDKS density matrix. Ω and $|X, Y\rangle$ are the solutions of the TDKS EVP (17). The normalization condition (18) can be used to assign a state in terms of excitations from occupied to virtual KS MOs. The weight of a one-particle excitation from the occupied orbital i to the virtual orbital a is

$$w_{ia} = X_{ia\sigma}^2 - Y_{ia\sigma}^2. \quad (19)$$

The configuration mixing reflects the change in the Coulomb and exchange-correlation potentials upon excitation. More elaborate methods to analyze transition vectors use transition natural orbitals [24] or attachment and detachment densities [25]. Denoting the electronic dipole moment operator by $\boldsymbol{\mu}$, the oscillator strength for the transition $n \leftarrow 0$ is given by

$$f_{0n} = \frac{2}{3} \Omega_n |\langle \boldsymbol{\mu} | X_n, Y_n \rangle|^2. \quad (20)$$

Similarly, the rotatory strength is

$$R_{0n} = \text{Im}(\langle \boldsymbol{\mu} | X_n, Y_n \rangle \cdot \langle X_n, Y_n | \mathbf{m} \rangle), \quad (21)$$

where \mathbf{m} denotes the magnetic dipole moment operator. $\boldsymbol{\mu}$ can be expressed in various forms, e.g., the dipole-length or the dipole-velocity form [26] which are related by a gauge transformation. Since the TDKS formalism is gauge invariant, the different forms of $\boldsymbol{\mu}$ lead to the same result in the basis set limit [15]. As expected for a response theory based approach, the oscillator strength and the rotatory strength satisfy sum rules. For example, the isotropic polarizability of the the ground state at frequency ω has the SOS expansion

$$\alpha(\omega) = \sum_n \frac{f_{0n}}{\Omega_{0n}^2 - \omega^2}. \quad (22)$$

This is true independent of the basis set and functional.

3. The “ Z vector” equation and the determining equations for W . They follow from the stationarity condition

$$\frac{\delta L}{\delta C_{\mu p \sigma}} = 0. \quad (23)$$

The Z vector equation is a static perturbed KS equation of the form

$$(A + B)Z = -R. \quad (24)$$

The expressions for R and W involve third order functional derivatives and are explicitly given in Ref. [17]. The difference between the excited and ground state density matrices is given by

$$P = T + Z, \quad (25)$$

where the “unrelaxed” part T contains products of the excitation vectors only. Z accounts for relaxation of the ground state orbitals; it can be of the same order of magnitude as T . The information contained in P is complementary to the information contained in the transition vector. The latter is related to matrix elements between the ground and excited state, while P is related to the *difference of expectation values* for the excited and the ground state. For example, $\text{tr}(P\boldsymbol{\mu})$ is the change of the dipole moment upon excitation from the ground state; by adding the ground state density matrix to P , excited state properties can be computed in this way. Population analysis or graphical representation of P can give insight in the re-distribution of the electronic charge due to the excitation process.

The remaining Lagrange multiplier W accounts for first-order changes in the energy due to changes in the overlap matrix. W is therefore an “energy weighted difference density matrix”, and is needed for gradient calculations only. The total gradient of L with respect to a perturbation ξ has the form [17]

$$L^\xi = \sum_{\mu\nu\sigma} h_{\mu\nu}^\xi P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} S_{\mu\nu}^\xi W_{\mu\nu\sigma} + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} (\mu\nu|\kappa\lambda)^\xi \Gamma_{\mu\nu\sigma\kappa\lambda\sigma'} + \sum_{\mu\nu\sigma} V_{\mu\nu\sigma}^{\text{xc}(\xi)} P_{\mu\nu\sigma} + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} f_{\mu\nu\sigma\kappa\lambda\sigma'}^{\text{xc}(\xi)} (X+Y)_{\mu\nu\sigma} (X+Y)_{\kappa\lambda\sigma'}; \quad (26)$$

h is the sum the kinetic and potential energy one-particle operators and V^{xc} is the static exchange-correlation potential. Γ is an effective two-particle density matrix that separates into two-index quantities. ξ may represent, e.g., a component of an external electric field, in which case all terms except the first are zero; or it may represent a nuclear coordinate. Parentheses indicate that derivatives need to be taken *only* with respect to basis functions; MO coefficient derivatives do not occur as a consequence of the $2n+1$ rule. L^ξ has nearly the same form as the ground state energy gradient [27], the definitions of P , Γ , and W being the main difference. Total excited state properties are obtained by simply adding the ground state contributions.

2.3. Approximate exchange-correlation functionals

There are different approaches to the construction of approximate functionals. Empirical functionals contain a large number of parameters fitted to a “training set” of accurate experimental or calculated data. Non-empirical functionals contain few or no fitted parameters and are designed to satisfy known constraints. Empirical functionals should be accurate for systems and properties contained in the training set, but they can fail for other systems. In contrast, non-empirical functional usually exhibit a more uniform accuracy [28]. The accuracy of approximate exchange-correlation functionals is limited by their form, i.e., there is a certain *maximum accuracy* that can be expected for local, semi-local, etc. functionals. The “perfect agreement” with experiment reported in some density functional studies should therefore rather give rise to concern, especially if highly parameterized or exotic functionals are used.

The most common and universally used approximation in TDDFT is the above-mentioned AA [29]. It replaces the time-dependent exchange-correlation potential by its static counterpart, evaluated at the time-dependent density. The resulting potential is instantaneous, in contrast to the exact one, which has a “memory” of all times $t' \leq t$. In response

theory, the AA makes the exchange-correlation kernel and all higher derivatives of the exchange-correlation potential independent of the frequency.

The AA has been considered uncritical for a long time. Only recently it has been clarified that the lack of higher excited states in TDDFT excitation spectra is a consequence of the AA [30]. This may be related to the failure of the AA in dissociating H_2 , where doubly excited states are important [31].

2.3.1. Local and semi-local functionals

Semi-local functionals have the form

$$E^{\text{xc}} = \int d^3r f(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}), \nabla\rho_\alpha(\mathbf{r}), \nabla\rho_\beta(\mathbf{r}), \dots). \quad (27)$$

In the local spin density approximation (LSDA), f depends on the spin densities at \mathbf{r} only. The LSDA is derived from the exchange-correlation energy per particle of a uniform electron gas, which has been accurately parameterized [32, 33]. For functionals of the generalized gradient approximation (GGA), f also depends on the gradient of the spin densities. Popular GGA functionals with few empirical parameters are Becke’s 1988 exchange functional [34] together with the correlation functional of Lee, Yang, and Parr (BLYP) [35], or Perdew’s 1986 correlation functional (BP86) [36]. The GGA of Perdew, Burke, and Ernzerhof [37] (PBE) is parameter free, while Hamprecht, Cohen, Tozer, and Handy (HCTH) have proposed an empirical GGA functional [38]. In meta-GGA functionals, f depends on additional local information such as the kinetic energy density or the Laplacian of the density. Examples are the 21 parameter meta-GGA of Van Voorhis and Scuseria (VS98) [39], or the non-empirical meta-GGA of Tao, Perdew, Staroverov, and Scuseria (TPSS) [28].

2.3.2. Hybrid functionals

Hybrid functionals interpolate between HF theory and semi-local functionals [18, 19]; the fraction of HF exchange is controlled by the exchange mixing parameter c_x . The exchange is treated as in HF theory, using non-local potentials. This interpolation leads to an error compensation for many properties. Popular hybrid functionals are, e.g., B3LYP [40], B3PW91 [19], or PBE0 [41].

2.3.3. Optimized effective potential (OEP) based functionals

Exact exchange (EXX) as a functional of the KS density matrix has the same form as HF exchange. Differences arise in the variation of the energy. In HF theory, the energy is minimized with respect to the *density matrix*. The resulting exchange potential is the well-known *non-local* exchange operator in HF theory, while it is a *local* multiplicative potential in KS theory. For a fixed density, this potential can be determined by an energy optimization procedure, as first shown for atoms by Talman and Shadwick [42]. Computation of the local exchange potential in molecules is a non-trivial problem [43], but there has been recent progress in developing more efficient methods [44, 45] and approximations [46–48]. Full OEP calculations of the frequency-dependent exchange kernel have been reported for solids, but not for molecules so far [49]; see Refs. [50, 51] for a review. In most TDDFT applications, KS orbitals and orbital energies from an OEP calculation are combined with adiabatic LSDA or GGA exchange-correlation kernels.

2.3.4. Asymptotic corrections

The exchange-correlation potentials of semi-local functionals decay too fast in the asymptotic region outside a molecule. In most cases, the decay is exponential, instead of the correct $-1/r$. As a result, diffuse excited states are often predicted too low in energy, and higher Rydberg excitations may be absent from the bound spectrum [52]. Various correction schemes have been suggested to remedy this problem [53–55]. These corrected potentials are not the derivative of any exchange-correlation energy functional, however. This does not affect vertical excitation energies, but makes a consistent definition of excited state total energies and properties difficult.

2.3.5. Current-dependent functionals

Some deficiencies of semi-local functionals can be cured by using the current density \mathbf{j} instead of the density. Vignale and Kohn have shown that the time-dependent exchange-correlation vector potential of weakly inhomogeneous systems possesses a gradient expansion as a functional of \mathbf{j} but not of ρ [56, 57]. Current dependent functionals capture macroscopic polarization effects in solids which are ultra-non-local in the density [58]. First applications to molecular excitation energies [59] show a somewhat mixed picture, however.

3. COMPUTATIONAL STRATEGIES

3.1. Basis set methods

As explained in the last section, performing a TDDFT excited state calculation amounts to finding the stationary points of the Lagrangian L . Introduction of a finite basis set (usually atom-centered) generates a finite number of MOs through the LCAO expansion (9). If the basis set is suitably chosen, the excited state energy may be well approximated by optimizing L on the corresponding subspace. We thus arrive at a *finite-dimensional* optimization problem which can be solved by matrix algebra. The basis set incompleteness can be checked by using hierarchical basis sets of different size, compare Sec. 3.3.

The steps necessary to compute excited state energy and gradients parallel the stationarity conditions for L discussed in Sec. 2.2.2. A summary is given in Table 1, including the scaling of the computational cost with the system size measured by N .

Table 1
Steps in an excited state energy and gradient calculation, formal and asymptotic scaling of computational cost.

	Scaling	
	Formal	Asymptotic
Ground state energy and wavefunction	N^4	N^2
Excitation energy	N^4	N^2
Relaxed density and gradient	N^4	N^2

The first step, solution of the ground-state KS equations in a finite basis set, is a standard procedure in quantum chemistry and needs no further discussion here. In the

second step, (approximate) excitation energies and transition vectors are calculated by solving the finite-dimensional TDKS EVP. Complete diagonalization of the electronic Hessian Λ scales as N^6 and is prohibitive for systems with more than 10 heavy atoms. In most applications, however, especially in larger systems, only the lowest excited states are of interest. By *iterative methods*, the lowest part of the spectrum of Λ can be calculated much more efficiently than by complete diagonalization.

Iterative methods minimize L by expanding the excitation vector on a subspace whose dimension is small compared to the full problem. One usually starts from unit vectors, i.e., the KS one-particle excitations. In each iteration, the best approximation to the excitation energy is calculated by a small diagonalization on the current subspace (Ritz step). The error is controlled by the norm of the residual which corresponds to the gradient of L . If the error is small enough, the process terminates; otherwise, the subspace is extended in the direction of the (preconditioned) gradient and a new iteration starts. Similar ideas can be found in the early work of Lanczos [60] and Hestenes and Stiefel [61] already, but it was only the preconditioning introduced by Davidson [62, 63] that made these iterative algorithms useful for quantum chemistry. The extension to the special EVPs occurring in response theory goes back to Olsen, Jensen, and Jørgensen [64]; in the meantime, several modifications have been suggested [65–68]. If “pure” functionals are used, it is favorable to transform the TDKS EVP to a symmetric problem of half the original dimension [69]; the latter is amenable to standard algorithms for symmetric-positive EVPs.

The time-determining step in all iterative methods is the computation of matrix-vector-products $|U, V\rangle = \Lambda|X, Y\rangle$, where $|X, Y\rangle$ is a subspace basis vector. This is most efficiently performed as

$$(U + V) = (A + B)(X + Y), \quad (28a)$$

$$(U - V) = (A - B)(X - Y), \quad (28b)$$

because the symmetry of $(A \pm B)$ (as a super-operator) and of $(X \pm Y)$ can be fully exploited. The diagonal contribution to $(A \pm B)$ resulting from the orbital energy differences, cf. Eqs. (13), is trivial to compute. The multiplication by the the remaining four-index integrals is best performed by transforming the vectors to the AO basis, in the spirit of direct CI methods [70] in an AO formulation [71, 72]. Denoting the transformed vectors by Greek indices, we have

$$(X \pm Y)_{\mu\nu\sigma} = \frac{1}{2} \sum_{ia} (X \pm Y)_{ia\sigma} (C_{\mu i\sigma} C_{\nu a\sigma} \pm C_{\mu a\sigma} C_{\nu i\sigma}). \quad (29)$$

With respect to the AO indices, $(X + Y)$ is a symmetric and $(X - Y)$ a skew-symmetric square matrix. After that, one computes

$$(U + V)_{\mu\nu\sigma} = \sum_{\kappa\lambda\sigma'} (2(\mu\nu|\kappa\lambda) + 2f_{\mu\nu\sigma\kappa\lambda\sigma'}^{\text{xc}} - c_x \delta_{\sigma\sigma'} [(\mu\kappa|\nu\lambda) + (\mu\lambda|\nu\kappa)]) (X + Y)_{\kappa\lambda\sigma'} \quad (30a)$$

$$(U - V)_{\mu\nu\sigma} = \sum_{\kappa\lambda\sigma'} c_x \delta_{\sigma\sigma'} [(\mu\kappa|\nu\lambda) - (\mu\lambda|\nu\kappa)] (X - Y)_{\kappa\lambda\sigma'}. \quad (30b)$$

Back-transformation finally yields the product vectors in the MO basis,

$$(U \pm V)_{ia\sigma} \rightarrow \frac{1}{2} \sum_{\mu\nu} (U \pm V)_{\mu\nu\sigma} (C_{\mu i\sigma} C_{\nu a\sigma} \pm C_{\mu a\sigma} C_{\nu i\sigma}). \quad (31)$$

The part resulting from the two-electron integrals is fully equivalent to a ground-state Fock matrix construction for a complex density matrix [65]. This means that highly efficient direct SCF techniques available for ground states can be carried over to excited state calculations with minimal modifications. Thus, in each iteration, only $O(N^2)$ non-zero two-electron integrals $(\mu\nu|\kappa\lambda)$ are calculated “on the fly”, i.e., they are completely or partly discarded after use and not stored. In contrast, an integral transformation would lead to an $O(N^5)$ scaling of CPU-time and $O(N^4)$ I/O, because $(A \pm B)$ is generally not sparse in the MO basis. The analogy to ground-state calculations also holds for the contribution arising from the exchange-correlation kernel. The four-index quantities $f_{\mu\nu\sigma\kappa\lambda\sigma'}^{\text{xc}}$ are never actually calculated; instead, the contributions to $(U + V)$ are formed directly on the quadrature grid and integrated, which is virtually equivalent to setting up the matrix of the ground-state exchange-correlation potential [17, 69]. For semi-local functionals, prescreening leads to a scaling of $O(N)$ for the exchange-correlation contribution to the matrix-vector-products $(U + V)$. The vector transformation steps (29) and (31) have a formal $O(N^3)$ scaling; however, if efficient linear algebra subroutines are used, the cost is negligible for systems with up to ca. 10000 basis functions.

For simulating electronic excitation spectra of larger systems, block iteration methods lead to dramatic further savings of computation time [73, 74]. In these methods, a number of states is treated simultaneously. This means that the two-electron integrals need to be calculated only once for all vectors of a block. In addition, block methods often show favorable convergence compared to single-vector methods.

Molecular point group symmetry can be exploited in the MO basis by Clebsch-Gordan reduction of MO products and in the AO basis by skeleton operator techniques [65, 74, 75]. This leads to an overall reduction of computational cost by approximately the order of the point group. Advantage can be taken of spin symmetry as well. For closed-shell singlet ground states, the TDKS EVP decomposes into two separate EVPs for singlet and triplet excitations. A restricted open shell scheme for high spin ground states has been proposed recently [76].

If first-order excited state properties are to be calculated, the Z vector equation (24) needs to be solved in the third step. This is best done iteratively again, using the techniques outlined above. Once the relaxed density matrices P and W have been obtained, excited state properties can be evaluated in almost the same manner as ground state properties. It is important that the thus obtained relaxed density matrices do *not* depend on the perturbation. The cost for computing analytical gradients of the excited state energy is therefore independent of the number of nuclear degrees of freedom. In contrast, numerical differentiation leads to a cost that increases linearly with the number of nuclei.

The cost for computing excited state energies and first-order properties differs from the cost for the corresponding ground-state calculations by a constant factor only. In conclusion, excited state geometry optimizations within the TDDFT framework are hence not significantly more expensive than conventional DFT ground state optimizations [17]. The prerequisite is, however, that the $2n + 1$ rule is used and full advantage is taken of

the similarity to efficient ground state algorithms.

3.2. Approximations and extensions

3.2.1. Efficient treatment of the Coulomb energy

As explained in Sec. 3.1, computation of the two-electron integrals $(\mu\nu|\kappa\lambda)$ is the bottleneck in larger TDDFT response calculations. For non-hybrid functionals ($c_x = 0$), these integrals contribute to the Coulomb part of the excitation energy only,

$$\begin{aligned} E_C[\rho_{0n}] &= \frac{1}{2} \sum_{\mu\nu\kappa\lambda\sigma\sigma'} (X + Y)_{\mu\nu\sigma} (\mu\nu|\kappa\lambda) (X + Y)_{\kappa\lambda\sigma'} \\ &= \frac{1}{2} \int d^3r d^3r' \frac{\rho_{0n}(\mathbf{r})\rho_{0n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (32)$$

The last expression is identical to the ground state Coulomb energy functional, evaluated at the spin-averaged transition density

$$\rho_{0n}(\mathbf{r}) = \sum_{\sigma} \gamma_{0n\sigma}(\mathbf{r}, \mathbf{r}) = \sum_{\mu\nu\sigma} (X + Y)_{\mu\nu\sigma} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \quad (33)$$

RI- J techniques for a fast evaluation of the ground state Coulomb energy [77, 78] can thus be carried over to excited state calculations in a straightforward manner.

The key idea of RI- J approximation is to introduce an auxiliary expansion of the density in a set of one-center functions $\chi_p(\mathbf{r})$ (usually atom-centered Gaussians) [79–83],

$$\tilde{\rho}_{0n}(\mathbf{r}) = \sum_p c_p \chi_p(\mathbf{r}). \quad (34)$$

The expansion coefficients c_p are determined by minimizing the error in the Coulomb norm

$$\|\rho_{0n} - \tilde{\rho}_{0n}\|_C^2 = \frac{1}{2} \int d^3r d^3r' \frac{[\rho_{0n}(\mathbf{r}) - \tilde{\rho}_{0n}(\mathbf{r})][\rho_{0n}(\mathbf{r}') - \tilde{\rho}_{0n}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|}. \quad (35)$$

This leads to the Coulomb energy in the RI- J approximation,

$$E_C[\tilde{\rho}_{0n}] = \frac{1}{2} \sum_{\mu\nu\kappa\lambda\sigma\sigma'} \sum_{pq} (X + Y)_{\mu\nu\sigma} (\mu\nu|p)(p|q)^{-1}(q|\kappa\lambda)(X + Y)_{\kappa\lambda\sigma'}. \quad (36)$$

In this expression only three- and two-center electron repulsion integrals occur, with products of basis functions replaced by auxiliary functions (denoted by labels p, q). In the auxiliary basis set limit, Eq. (36) is formally obtained from Eq. (32) by inserting the identity. The choice of the Coulomb metric implies that the error $E_C[\rho_{0n}] - E_C[\tilde{\rho}_{0n}]$ is positive and quadratic in the error in the density. This *variational stability* ensures that good accuracy can be achieved with relatively small auxiliary basis sets.

The RI- J approximation has several computational advantages. First, the calculation of four-center integrals $(\mu\nu|\kappa\lambda)$ that formally scales as N^4 is replaced with two N^3 steps. By means of integral pre-screening, the scaling can be further reduced to N^2 , as in the conventional case; the pre-factor is much lower, however. Secondly, a large amount of

integrals $(\mu\nu|p)$ can be pre-computed and stored in memory. The inverse $(p|q)^{-1}$ is never actually calculated; instead, linear equation systems are solved using the Cholesky decomposition of $(p|q)$ [84]. This very fast $O(N^3)$ step is performed once before the iteration starts and has almost no effect on total computation times for systems that are currently feasible. Speedups of a factor of 10 and more are achieved for the Coulomb contribution to the excitation energy compared to conventional methods [85]. This leads to a significant reduction of total timings for large systems, where the exchange-correlation part becomes less important due to its favorable $O(N)$ scaling.

Auxiliary basis sets developed for ground state calculations [77, 86–90] are sufficient for most TDDFT applications, although in some cases additional diffuse basis functions must be included. For excitation energies RI- J errors of less than 0.005 eV are observed for valence excitations, whereas for Rydberg excitations somewhat greater deviations up to 0.05 eV are found. These deviations are usually much smaller than both errors due to the incompleteness of the one-particle basis set and due to the use of approximate functionals, compare Secs. 3.3 and 4).

TDDFT implementations using fitting basis sets are available, e.g., in the deMon [91], TURBOMOLE [85], and PARAGAUSS [22, 92] program packages which make use of Gaussian auxiliary basis functions. Basis sets of Slater-type (STO) are employed in the ADF [67, 93, 94] program. Some of these implementations use other norms for the auxiliary expansion, e.g., the overlap norm, or norms based on the exchange-correlation kernel f^{xc} or the full TDDFT response kernel instead of the Coulomb interaction [22]. A similar resolution of the identity approach has been developed for non-local HF exchange [87]. This RI- JK approach can be useful for TDDFT calculations with hybrid functionals [95], but is more demanding and requires larger auxiliary basis sets than the RI- J method. Typical speedups are in the range of 2 – 4 compared to the full calculation of four-center integrals.

Analytical gradient calculations for excited states can take advantage of the RI- J approximation as well [96]. RI- J may be used in the determination of excitation energies and transition vectors $(X \pm Y)$ and in the iterative solution of the Z vector equation (24). The calculation of excited state gradients can be carried out along the same lines as for ground state gradients. The total computational effort for excited state optimizations is reduced by at least a factor of 4-6 by the RI- J approximation. This allows to perform excited state optimizations on medium-size and large molecules with more than 100 atoms. RI- J errors in optimized bond lengths and angles amount to less than 0.5 pm and 1 degree, respectively. For adiabatic excitation energies, RI- J errors of 0.01-0.02 eV are found.

3.2.2. The Tamm-Dancoff-approximation (TDA)

The TDA amounts to constraining $Y \equiv 0$ in the variation of L . As a result, the TDKS EVP reduces to the symmetric-positive EVP

$$AX^{\text{TDA}} = \Omega^{\text{TDA}} X^{\text{TDA}}. \quad (37)$$

For TDHF, the TDA is equivalent to the configuration interaction singles (CIS) method, where the excited states are determined by diagonalizing the singles part of the stationary Hamiltonian. The TDA was introduced to TDDFT by Grimme [97], who used additional

empirical parameters to correct some of the systematic errors; the above form (37) is due to Hirata and Head-Gordon [98].

A frequently used motivation for the TDA is its apparent computational advantage due to the reduction of dimensionality. This argument overlooks that, in an integral direct algorithm, the cost for computing a matrix-vector-product AX is approximately the same as the cost for computing the *two* matrix-vector-products $(A + B)(X + Y)$ and $(A - B)(X - Y)$. This is due to the lack of symmetry of the AO-transformed vector $X_{\mu\nu\sigma}$, which is neither symmetric nor skew-symmetric. In fact, in an integral-driven algorithm, where only non-redundant integrals $(\mu\nu|\kappa\lambda)$ are calculated in the innermost loop, AX has to be computed according to [65]

$$AX = \frac{1}{2}[(A + B)X + (A - B)X]; \quad (38)$$

this involves approximately the same operation count as the simultaneous formation of $(A + B)(X + Y)$ and $(A - B)(X - Y)$. The vector-vector operations performed in the MO basis are much less expensive and affect total CPU timings only marginally.

A positive aspect of the TDA is its improved stability. It is well known that closed-shell HF solutions may be unstable with respect to a spin-symmetry breaking [99]. The resulting *instabilities* lead to negative or imaginary excitation energies and a breakdown of the response formalism in its usual form. Triplet instabilities are a common limitation in TDHF theory, especially at geometries that differ significantly from the ground-state minimum. The KS reference is generally less susceptible to instabilities [100]; nevertheless, there is still a tendency to underestimate triplet excitation energies. The TDA alleviates this problem, because the variational constraint leads to systematically higher excitation energies.

Transition moments are somewhat ill-defined in the TDA because of its lack of gauge invariance. For example, the length and velocity forms of the transition dipole moment may differ even in the basis set limit. Furthermore, the TDA does not satisfy the usual sum rules. These problems do not affect singlet-triplet excitations, where the transition moments vanish due to spin symmetry.

3.2.3. Other approximations

Many approximations commonly made in ground state calculations are easily carried over to TDDFT. Examples are the frozen core approximation or the use of effective core potentials. We also mention semi-empirical approximations such as tight-binding DFT [101] here. The single-pole approximation [23, 102] is mainly used in physics and corresponds to first-order perturbation theory for the excitation energies starting from the KS orbital energy differences as zeroth order. It is often appropriate in small systems but breaks down in situations where excited states are nearly degenerate and strong configuration mixing occurs.

3.2.4. Solvent effects

Electronic absorption and CD spectra usually exhibit a marked solvent dependence. A common approach to include these effects in quantum chemical calculations is based on classical electrostatic solvent models, e.g., the polarizable continuum model (PCM) [103] or COSMO [104]. In these models, the solvent is approximated by a polarizable

continuum, while the solute molecule is placed in a cavity, whose dielectric constant is set to one. The presence of the solvent leads to an additional external potential which depends itself on the charge density of the electrons.

An extension of the PCM to TDDFT vertical excitation energies has been reported by Cossi and Barone [105]. The computed solvent shifts were found to be fairly accurate in benchmark applications to small molecules [106]. Solvent effects on excited state geometries have been studied in an approximate TDDFT framework by Tomasi and coworkers [107]. A hybrid Car-Parrinello quantum mechanical/molecular mechanical (QM/MM) approach which includes the solvent explicitly has recently been applied to the ground and first excited singlet state of acetone in water [108].

3.3. Basis set effects

Flexible Gaussian basis sets developed for ground states are usually well suited for low-lying valence excited states. Split valence basis sets with polarization functions on all non-hydrogen atoms such as 6-31G* [109] or SV(P) [110] are useful in exploratory calculations or larger applications. These basis sets systematically overestimate excitation energies by several tenths of an eV, and transition moments are qualitative only. Exceptions are larger planar systems, where transitions in the molecular plane can be accurate in small basis sets already. For states with Rydberg character and higher excitations, diffuse augmentation is necessary. Usually one adds atom-centered or molecule-centered primitive Gaussians whose exponents are determined by downward extrapolation or by optimization for atomic anions [111]. In general, diffuse functions should be used sparingly, to avoid imbalance and unnecessary computational cost. Continuum excitations show poor or no basis set convergence [52] and require special techniques. The KS ionization threshold should therefore always be checked in TDDFT excited state calculations. The basis set dependence of excited state structures, dipole moments, and force constant parallels that observed in ground states [74]; for example, C–C bonds lengths are usually overestimated by ca. 1 pm in split-valence basis sets. For most applications, triple zeta valence basis sets with two sets of polarization functions, i.e., *2d1f* for first-row elements, yield basis set errors well below the systematic errors of current functionals. Examples of triple zeta valence basis sets are the segmented contracted TZVPP [112], or Dunning’s *cc-pVTZ* [113], which uses generalized contractions. Larger basis sets are necessary for benchmark and basis set convergence studies. For DFT total energies, basis set convergence within “chemical accuracy” is reached at the quadruple zeta valence level [114].

3.4. Examples

A number of commercial quantum chemistry programs support the calculation of TD-DFT vertical excitation energies, e.g., ADF [115], CADPAC [116], deMon [91], Gaussian [117], Q-Chem [118], PARAGAUSS [22], and TURBOMOLE [119]. The demonstrative CPU timings in Table 2 are from Ref. [74] and were obtained using TURBOMOLE V5-4. The RI-J method was employed for the cases denoted “RI-TDDFT”; no other approximations were made.

The examples in Table 2 show that TDDFT calculations are practicable for systems with several hundreds of atoms and several thousands of basis functions, even on low-end personal computers. TDDFT is thus becoming a challenge for semi-empirical methods, which have almost exclusively been used for applications of this size.

Table 2

CPU timings (hours) for the calculation of excitation and CD spectra. p is the number of (symmetry allowed) excitations including degeneracy, N_{BF} is the number of Cartesian basis functions. The computer platforms (P) include a 1.2 GHz Athlon PC (A) and a 440 MHz HP J5000 (B) workstation (both single processor).

System	Sym.	Method	Basis/Grid	N_{BF}	p	CPU	P
Tris(alanine)-Co ^{III}	C_3	B3LYP	SVP/m3	386	100	12:04	B
Cu-phthalocyanine ^a	D_{4h}	B3LYP	SVP/4	706	90	40:24	B
Tetrathia-[7]helicene	C_2	B3LYP	SVP(s)/3	482	50	30:13	B
Fullerene C ₅₄₀	I_h	BP/RI	SVP/m5	8100	3	19:17	B
“Cd ₁₀ Se ₁₆ ” ^b	T	BP/RI	SV(P)/m3	2804	300	128:04	A
Vancomycin	C_1	BP/RI	SV(P) ^c /m3	1294	100	46:08	B
Methylcobalamine	C_1	BP/RI	SV(P) ^d /m3	1600	100	62:18	A

^aOpen shell

^bCd₁₀Se₄(SePh)₁₂(PⁿPr₃)₄

^cOptimized SZ basis sets on all weakly polarized alkyl und phenyl moieties

^dLarger TZVDP+f basis set for cobalt

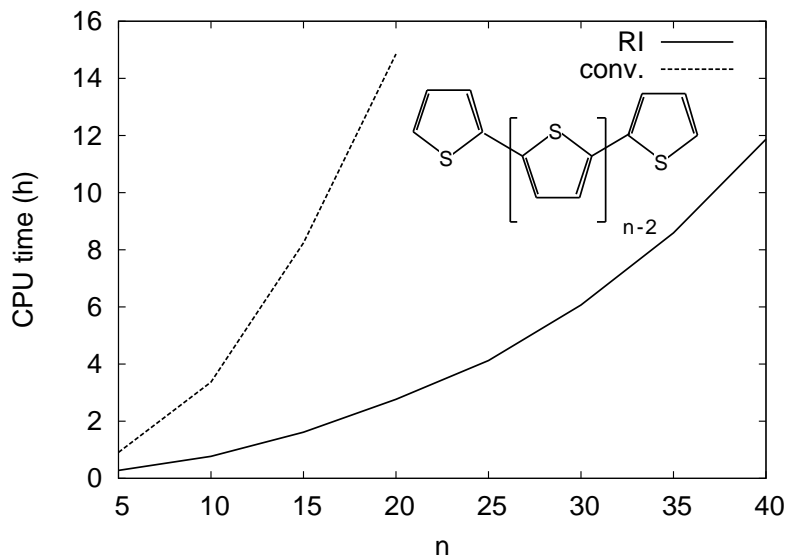


Fig. 1. CPU time for computing a single-point excited state energy plus gradient with and without the RI- J approximation as a function of the number of thiophene rings n . We used the BP86 functional and a TZVPP basis set. The calculations were performed on a 1.2 GHz Athlon PC.

The geometry optimization of the 2^1A state of chlorophyll a may serve as an example for the efficiency of the RI- J approximation, as implemented in TURBOMOLE. The BP86 functional and a SV(P) basis set were used, leading to a total of 1114 Cartesian basis functions. The overall calculation took 13 geometry cycles starting from the optimized ground state geometry and required 29:57 h of CPU time on a 2.4 GHz Pentium IV PC.

Fig. 3.4 displays the scaling of computational cost for single-point excited state gradient calculations with and without the RI- J approximation. We consider α , α' -oligothiophenes with increasing chain length. Both methods show the expected N^2 scaling, but with different pre-factors. For the larger members of the series, the RI- J approximation leads to a reduction in total computation times of a factor of 4-6.

4. VALIDATION

4.1. Vertical excitation and CD spectra

Semi-local functionals predict low-lying valence excitation energies with errors in the range of 0.4 eV [69, 91, 98, 120–127]. There is a systematic underestimation [69] which may be due to the missing integer derivative discontinuity [128]. This underestimation is larger for singlet-triplet excitations [129, 130]. Hybrid functionals yield smaller but less systematic errors, at somewhat higher cost. Contemporary TDDFT methods certainly cannot claim “chemical accuracy” (errors ≤ 0.05 eV), but they are often accurate enough to make useful predictions. Calibration with accurate experimental or theoretical results for small systems is always recommendable. The domain of TDDFT are larger systems, where experimental inaccuracies may be comparable to the systematic errors of TDDFT, and correlated *ab initio* methods are (still) too expensive. With errors of 1-2 eV and more, traditional CIS and TDHF methods are considerably less accurate than TDDFT, despite similar or higher computational requirements.

There are situations where semi-local functional tend to produce much larger errors, though. Lower-lying diffuse states are often too low in energy, and higher Rydberg states are spuriously unbound [52, 131]. Similarly, the excitation energies of charge transfer (CT) and ionic states may be considerably underestimated [128, 132, 133]. In conjugated aromatic compounds [134] and polymers [135], the error in CT excitation energies increases with the chain length, and excitons may be erroneously unbound [136].

These failures may partly be traced to the self-interaction problem of semi-local functionals which has been known for a long time [137]. The classical Coulomb energy contains self-interaction which semi-local functionals do not cancel properly in strongly inhomogeneous systems. As a result, an electron “sees” the effective charge of N rather than $N - 1$ other electrons in the asymptotic tail of the density. The asymptotic correction schemes mentioned in Sec. 2.3.4 partly remedy this problem by imposing the correct $-1/r$ -behavior on the exchange-correlation potential. They do *not* improve the description of CT states, however. Correction schemes have been devised to estimate the missing derivative discontinuity in CT excitation energies from Δ SCF calculations [132, 133]. At present, these approaches are mainly of diagnostic value because they depend on assumptions such as complete charge separation that may not be satisfied in many situations.

The EXX methodology offers a more fundamental solution to the self-interaction problem. EXX potentials are self-interaction free and lead to a correct description of diffuse

states [138–140], and optical properties of conjugated polymers are improved [141]. Efficient methods to generate exact [44, 45] or approximate [46–48] EXX potentials for molecular systems are available. So far, they have been combined with adiabatic LSDA or GGA kernels; the EXX kernel is frequency-dependent and applications have been reported for solids only [49].

The dilemma of the EXX method is that, although it solves the Coulomb self-interaction problem, it does not improve consistently upon semi-local functionals for all systems and properties. For example, excitation energies of valence excited states are not better or even worse [138, 140]. Unfortunately, the error cancellation between approximate exchange and correlation in semi-local functionals is lost when exact exchange is combined with semi-local correlation functionals. Hybrid functionals compromise between these extremes by using only a fraction of exact exchange. While this is not a general solution, it works often surprisingly well even for CT [142] and diffuse [143] states. In the long term, the development of correlation functionals compatible with exact exchange remains desirable.

Oscillator strengths of well-separated states are usually predicted with errors in the 10% range [125]. They can be qualitatively wrong for strongly coupled states (as in most other methods). As the excitation energy approaches the KS ionization threshold, i.e., the negative HOMO energy, the density of states increases and a reliable assignment of individual transitions becomes impossible. This can be a major limitation in applications, especially to smaller systems and negative anions, because GGA potentials are too repulsive which results in too few bound states, as explained above. In other cases, one finds spurious intruder states which “steal” intensity from adjacent transitions of the same symmetry [144]. Nevertheless, apart from the technical difficulties associated with continuum states, the overall shape of the computed spectra is often accurate [145]. This is also true if states with strong double excitation character are involved [30]. *Pure* double excitations are entirely missing in the TDDFT spectra [129], as a consequence of the AA.

Trends observed for calculated rotatory strengths are generally similar to those observed for oscillator strengths [73, 146]. Rotatory strengths of individual transitions may even have the wrong sign; but the overall CD spectra are often fairly accurate. The use of gauge origin invariant London orbitals does not seem to be necessary [147]. The simulation of CD spectra by TDDFT calculations is becoming increasingly popular as an inexpensive method to determine the absolute configuration; additional information is provided by optical rotations which can be calculated as well [148–151]. TDDFT works for inherently chiral chromophores [152] and transition metal complexes [153, 154], but has problems with weakly disturbed, inherently achiral chromophores and systems with Rydberg-valence mixing [155].

4.2. Excited state properties

As analytical gradients of the excited state energy have become available only recently [17, 156–158], the literature on excited state properties obtained with TDDFT is still limited. A comparison with accurate spectroscopic data for small systems shows that TDDFT excited state structures, dipole moments, and vibrational frequencies are of similar accuracy as the corresponding DFT ground state properties [17]. Case studies for other systems [159, 160] and correlated *ab initio* results [161] corroborate this finding, which is somewhat unexpected in view of the relatively large errors in the excitation en-

ergies. Obviously, properties such as structures or dipole moments are less sensitive to deficiencies of current exchange-correlation functionals, e.g., self-interaction. The traditional CIS method, which has almost exclusively been used for geometry optimization of excited states in larger systems, is considerably less accurate at similar or even larger computational cost.

Another significant advantage of TDDFT over HF-based methods for excited states is the enhanced stability of the KS reference compared to the HF reference, as discussed in Sec. 3.2.2. As a result, even excited state minima distant from the ground state minimum are mostly reasonable with TDDFT. Adiabatic excitation energies thus show basically the same error pattern as vertical excitation energies.

Excited state vibrational frequencies can be used to identify the structure of excited states by comparison with, e.g., time-dependent infrared (TIR) or time-dependent resonance Raman (TRR) spectra from pump-probe experiments [162]. This is a promising combination, because TDDFT is applicable to fairly large systems and the information contained in the experimental spectra is difficult to interpret. In addition, the vibronic fine structure of UV spectra can be simulated within the Franck-Condon and Herzberg-Teller approximations. Applications to aromatic hydrocarbons show a very encouraging agreement with experiments [163].

4.3. Excited state dynamics

Early work by Casida [164] and Domcke and coworkers [165] indicated that TDDFT can provide qualitatively correct excited state reaction paths. The validation is difficult and has to rely almost exclusively on accurate *ab initio* results. For the conical intersection in the retinal model Z-penta-2,4-dieniminium, TDDFT and CASPT2 (complete active space self-consistent field plus second order perturbation theory) single-point results are in agreement, while deviations have been reported for other systems [166]. A limitation most studies is that the calculated reaction paths do not correspond to minimum energy paths (MEPs), i.e., the internal degrees of freedom other than the reaction coordinate are not relaxed. The first full MEP calculations using TDDFT have been performed only recently [162]. For an adequate treatment of conical intersections and excited state dynamics, non-adiabatic coupling needs to be taken into account [167, 168]. It seems unlikely that present functionals are accurate enough for predicting, e.g., barrier heights, but definite conclusions will have to await further studies.

5. APPLICATIONS

5.1. Aromatic compounds and fullerenes

Aromatic compounds are among the most frequently investigated molecules in TDDFT studies. Several papers on singlet and triplet excitation energies of condensed polycyclic aromatic hydrocarbons (PAHs) [92, 169–172] have appeared. In a recent study Grimme and Parac [134] have pointed out that the energy of the ionic L_a states [173] is significantly underestimated by common functionals. PAHs and their cations have also attracted interest due to their proposed occurrence in the dark interstellar matter [127, 174–177].

Chiroptical properties of a series of helicenes have been investigated in a joint experimental and theoretical study [73]. The simulated CD spectra are accurate enough to assign the absolute configuration and can even be used to distinguish derivatives with

substituents coupling to the aromatic π system. CD spectra calculated with the DFT/SCI method have been used by Grimme and co-workers for structure elucidation of paracyclophanes [178]. Recently, the absolute configuration of enantiopure 9,9'-biathryls could be assigned by means of CD calculations [179].

For small aromatic heterocycles accurate excited state calculations with correlated *ab initio* methods are available. TDDFT studies focus on solvation effects [180, 181], excited state dynamics [182–185], and larger systems [186–191]. Moreover, TDDFT calculations complement experimental investigations of newly synthesized ring systems like tetrathiavalene [192, 193] and trithiapentalene [194]. Other recent TDDFT studies deal with indole derivatives related to tryptophane metabolism and melanin formation [195, 196]. Laaksonen and co-workers [197] have investigated photochemical properties of urocanic acid, a human skin chromophore which plays a role in photo-immunosuppression and skin cancer. Mechanisms of photoisomerization of prototypical molecular switches azobenzene [198, 199] and stilbene [200, 201] have been the subject of other studies. Finally, the biological activity of the naturally occurring heterocycles luciferin [202] and flavins [203] has been investigated with TDDFT. Luciferin is responsible for the bioluminescence of fireflies, while flavins play a role in hydrogen transfer in cells.

So far, the only practicable route to prepare pure fullerenes is based on soot extraction. Because of the extremely small yields, electronic absorption spectroscopy is, besides NMR measurements, the most important method for the characterization of fullerenes. Apart from a uniform red-shift, TDDFT using GGA functionals predicts the absorption spectra of large gap fullerenes with surprising accuracy [204]. Small gap fullerenes are highly reactive and can presently only be studied theoretically. For example, of the seven isomers of C_{80} obeying the isolated pentagon rule, only three have a large gap, and two of those have been observed [205]. Other studies focus on functionalized and substituted fullerenes [206, 207], carbon nanotubes [208] and sheets [209, 210]. Lower symmetric larger fullerenes frequently exhibit inherent chirality. In contrast to semi-empirical methods, TDDFT is well suited to determine the absolute configuration of chiral fullerenes, as has been shown for D_2-C_{84} [152] as well as C_{76} and C_{78} isomers [74]. TDDFT calculations on C_{84}^{2-} have been used to assign the photoelectron spectrum of stable C_{84} dianions [211].

5.2. Porphyrins and related compounds

Porphyrins, phthalocyanines, porphyrazines, and similar heterocyclic systems show a variety of optical and photochemical properties that are of interest from a biochemical as well as a technological point of view. The first rationale of the characteristic features observed in the absorption spectra of porphyrins was given by Gouterman [212, 213] in 1961. It is based on a simple perimeter model for [18]-annulene, the basic building unit of porphyrins. In Gouterman's scheme two energetically close pairs of orbitals, the two highest occupied molecular orbitals (HOMO and HOMO-1) and the two lowest virtual MOs (LUMO and LUMO+1), are involved in the lowest singlet transitions and are responsible for the so-called Q- and B-bands of porphyrins.

For the free base porphyrin, the weaker pair of Q-bands (Q_x and Q_y) is found in the visible region whereas the substantially more intensive B-band (Soret band) is located in the near UV, see Fig. 5.2. The Q_x and Q_y bands were ascribed to the HOMO \rightarrow LUMO transition and the antisymmetric combination of HOMO \rightarrow LUMO+1 and HOMO-1

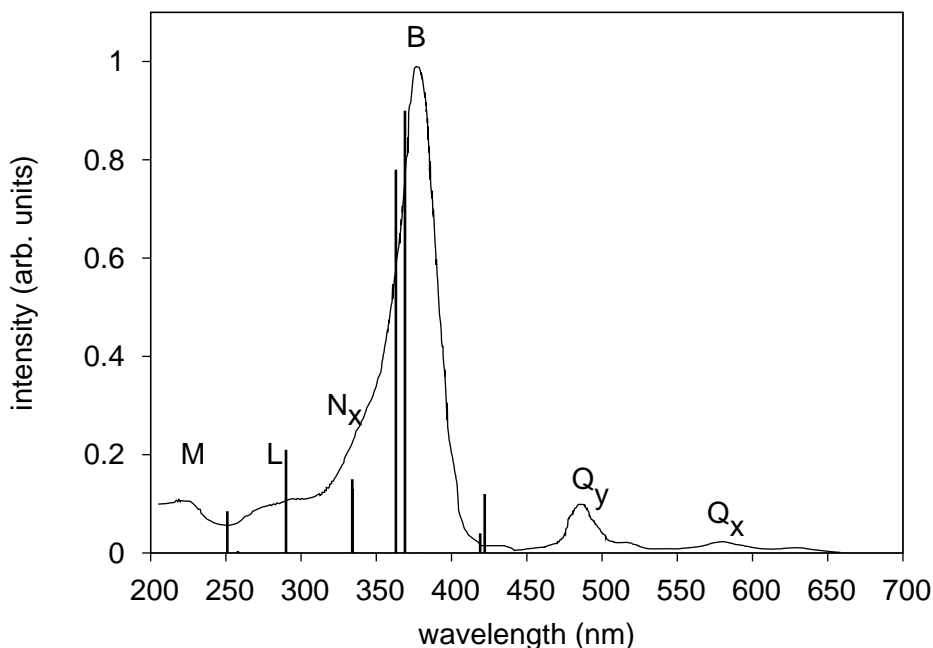


Fig. 2. The absorption spectrum of free base porphyrin. The experimental spectrum is from Ref. [214]. Calculated BP86/aug-SVP oscillator strengths [215] are indicated by sticks.

→ LUMO transitions, respectively. The symmetric combination of the latter two was considered as the origin of the Soret band. Porphyrin derivatives and analogues exhibit characteristic energy shifts and intensity patterns in the same energy range. The first TDDFT results on free base porphyrin were reported by Bauernschmitt and Ahlrichs [69] and later confirmed by Scuseria and co-workers [66]. Subsequent studies by van Gisbergen, Baerends and co-workers and by Sundholm addressed the validation of the four-orbital model of Gouterman for the free base porphyrin and the assignment of its UV/VIS spectrum [215–218]. Investigations by Parusel and co-workers employed the DFT/SCI [219] and DFT/MRCI methods [220] for the same purpose.

While a correspondence to the Gouterman model can be established for the Q bands, the origin of the intense B band is still under discussion. It appears that lower occupied orbitals are significantly involved in these transitions [215, 217], and a non-negligible contribution from double excitations is suggested from DFT/MRCI results [220]; thus, the simple four-orbital model does not hold. A similar picture emerges for porphyrazine [217, 221], corrphycene [222] and corrin [223] molecules where Gouterman’s model provides a rough description of low-lying electronic transitions. Positions of electronic excitations in porphyrins are further strongly affected by conformational flexibility of the macrocycle, deviations from planarity leading to red shifts of Q- and B-bands. The suggestion that nonplanarity of hemes in hemoproteins and photosynthetic proteins may influence their biological activity [224] stimulated much research on saddled and ruffled forms on porphyrins. Porphyrin diacids [225, 226] and complexes bearing aromatic substituents

[227–230] have been investigated as well.

Porphyrinoid systems have a tendency to form chelate complexes with various metal cations. Two large groups of complexes can be distinguished by their spectral behavior, denoted regular and irregular porphyrins by Gouterman [213]. Main group and closed-shell transition metal cations form regular complexes that largely resemble the parent macrocycles because the contribution of the metal to the frontier orbitals is small. This was shown by Nguyen, Baerends, and co-workers for Zn^{II} [231–235] and by Sundholm for Mg^{II} complexes [236]. In irregular metal complexes incomplete d -shells of transition metal cations interact strongly with the π -system of the ligand; substantially different optical properties [237–243] result. The most important representatives of this class are iron and cobalt complexes which are closely related to heme [244, 245] and vitamin B_{12} [246, 247].

5.3. Transition metal compounds

For calculations of optical properties of transition metal complexes, TDDFT is often the method of choice. In most cases the accuracy of TDDFT is sufficient for an assignment of excitations in closed-shell oxide, carbonyl and cyclopentadienyl complexes [121, 248–250]; hybrid functionals do not always lead to an improvement for these systems. Ligand field d to d transitions appear at too high energies as a result of self-interaction error, as Autschbach and co-workers have shown for Co^{III} and Rh^{III} complexes [154]. Difficulties are encountered for small open-shell molecules such as ScO or VO [251, 252]. The diversity of photophysical and photochemical properties of transition metal complexes is reflected in TDDFT investigations on this class of compounds. Possible applications in photocatalysis and solar energy conversion have triggered research on complexes of copper [253, 254], chromium [255], ruthenium [256, 257], palladium [258], platinum [259] and rhenium [260] with aromatic heterocyclic ligands as 9,10-phenanthroline (phen), α, α' -bipyridyl (bipy) or dipyrido[3,2- a :2',3'- c]phenazine (dppz). Dissociation and rearrangement dynamics upon photoexcitation has been discussed in connection with $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ [261, 262], $[\text{Cr}(\text{CO})_5\text{L}]$ and $[\text{Fe}(\text{CO})_4\text{L}]$ [263], as well as on $[\text{Ru}(\text{PH}_3)_3(\text{CO})(\text{H}_2)]$ complexes [264]. The catalytical activity of titanium complexes for polymerization and oxidation reactions has motivated several studies on titanocenes [265, 266] and alkoxy complexes [267]. Optical properties and bond dissociation of alkylplatinum complexes are the subject of a recent study by van Slageren and co-workers [268]. TDDFT calculations for neutral dithiolene complexes of nickel, palladium, and platinum have explained the uncommon properties of these compounds, especially the presence of an exceedingly strong absorption in the near IR region [269]. Other studies investigate the photophysics and the luminescence behavior of cyclometalated complexes of rhodium [270] and iridium [271].

5.4. Metal and semiconductor clusters

Metal clusters differ substantially in their properties from the bulk phase [272, 273] and have received much attention in connection with possible applications in nanotechnology and heterogenous catalysis. Experimental structure determination is a difficult task even for small clusters, and theoretical results are particularly helpful. Flexible structures, a large number of competing minima, and low-lying excited states are difficult challenges for all electronic structure methods. Most theoretical work therefore address the most simple class of metal cluster compounds, alkali metal clusters, for which reliable experimental data as well as accurate quantum chemical calculations [273, 274] exist. TDDFT

applications on alkali metal clusters range from simple jellium [275–279] to full TDDFT calculations employing GGA functionals [280–282]. Comparison with available experimental data indicates a good accuracy of TDDFT results with typical errors of 0.1–0.2 eV or less in excitation energies [283–285]. For the dimers Li_2 , Na_2 and K_2 , experimental vertical excitation energies are overestimated by TDDFT [281], in contrast to the usual behavior of the method. Photoabsorption spectra are reproduced satisfactorily as well [285–287]; finite temperature effects have been investigated by molecular dynamics simulations [288, 289]. Similar studies have been performed for Al clusters [290, 291].

Coinage metal (Cu, Ag, Au) clusters are more complicated due to the presence of rather polarizable d -electrons. Very little direct structural information is available from experiment. Of particular interest is the transition from the planar structures that are the most stable isomers for small clusters to bulk-like three-dimensional aggregates [292]. While the simple jellium model does not perform very well in this case, the polarizable cluster core approximation [293–295] or full TDDFT calculations [296–298] provide better results for photoabsorption spectra. Nevertheless, transitions with $s \rightarrow d$ character are notoriously in error, which is a consequence of self-interaction [137]. In summary, TDDFT absorption spectra can give useful hints, but are presently *not* accurate enough for a unique determination of the geometric structure of most metal clusters.

The band gap of semiconductor clusters can be altered over a wide range by varying the particle size; this makes them suitable materials for optoelectronic devices [299]. Recent TDDFT investigations have addressed optical properties of silicon [283, 287, 300–305], gallium arsenide [287], as well as zinc sulfide, cadmium selenide, and related 12–16 clusters [306–311]. Most studies focus on the size dependence of the optical gap. With increasing cluster size the band gap is reduced as a result of quantum confinement, e.g. for hydrogenated Si clusters from 3.8 eV for $\text{Si}_{47}\text{H}_{107}$ to 2.5 eV for $\text{Si}_{147}\text{H}_{247}$ [300]. Another important factor is the constitution of the cluster surface, with abstraction of hydrogen or oxidation leading to a substantial decrease of the absorption edge [299]. The definition of the optical gap is not straightforward, however, since the lowest electronic transitions are very weakly allowed in large clusters. Within these limitations both LSDA and gradient corrected functionals yield results in good agreement with experimental data.

5.5. Organic polymers

Two different theoretical approaches have been used for polymers: solid state methods employing periodical boundary conditions, and oligomer methods considering discrete fragments of increasing size. For calculations of excitation energies of organic polymers, the latter seems to be more widespread, although a LCAO-crystalline orbital implementation of excitation energies of extended systems has been reported [312, 313]. For oligomer methods, the convergence of the calculated properties to the bulk limit and the quality of extrapolated properties are of primary interest. Several papers by Ratner, Zojer, and co-workers summarize computational results on different classes of polymers [314, 315], e.g., polyenes, polythiophenes, and polyphenylenes. From these results, the authors concluded [316] that extrapolation techniques are capable of providing correct band gaps for the polymers. However, empirical extrapolations with respect to $1/n$, where n is the number of monomer units, may show significant systematic errors. Cai and co-workers [135] note a tendency to spurious metallic behavior and wrong ground state multiplicities in large

conjugated π -systems. For polyenes the relative stability of 1^1B_u and 2^1A_g states (in C_{2h} symmetry), which is of importance for carotenoids of the light harvesting complex, has been extensively discussed [166, 317–319]. Polythiophene [320–326] and polypyrrole [327, 328] polymers are important industrial materials for optoelectronic devices such as light emitting diodes (LEDs) have been the subject of numerous TDDFT studies.

5.6. Charge and proton transfer

The geometric and electronic structure of a molecule can significantly change upon photoexcitation. Transfer of charge or protons are among the most simple photochemical reactions, and excitation energy transfer plays a fundamental role for the photosynthesis. In work of Parusel, Grimme, and others, intramolecular charge transfer (ICT) in donor-acceptor substituted aromatic systems was investigated by TDDFT [329], DFT/SCI [330, 331], and DFT/MRCI [332–334] methods (see Ref. [329] for an overview). Most of the studies addressed 4-(N,N)-dimethylaminobenzonitrile (DMABN), a prototypical dual fluorescent compound showing a strong emission from the ICT state in polar solutions. In extensive studies by Jamorski and co-workers [142, 335–337], the accuracy of TDDFT for exploration of intramolecular charge transfer phenomena has been assessed, and a classification for the emission properties of these compounds was presented [338, 339]. A definite assignment of the structure of the two lowest singlet states has recently been given by means of TDDFT calculations [162] and confirmed by coupled cluster calculations [340]. Further investigations have dealt with solvent effects and photophysical properties of donor-substituted pyridine derivatives [341, 342].

Excited state proton transfer phenomena have been the subject of a number of TDDFT studies. So far, excited state proton transfer in salicylic acid and related aromatic compounds [165, 343–346] as well as in 7-azonindole-water complexes [347] has been investigated.

5.7. Biologically relevant systems

Most molecules of biological relevance are a challenge due to their size. Calculations of optical properties of chlorophylls and bacteriochlorophylls by Sundholm [144, 236, 348, 349] and Yamaguchi [350, 351] showed that good accuracy can be achieved with the BP86 and B3LYP functionals. Different aspects of the interaction between chlorophyll molecules and carotenoids and of the dynamics in the photosynthetic apparatus have been extensively studied by Dreuw, Fleming and co-workers [317, 352–354]. Pullerits and co-workers have investigated the dependence of excitation energies of bacteriochlorophyll on the local environment represented by a uniform electric field [355]. The dissociation dynamics of CO-hemoglobin complexes has recently been studied by Head-Gordon and co-workers [244, 245] who showed that excitation into the $5^1A''$ and the $3^1A'$ states of the complex leads to repulsive interaction and dissociation of the CO molecule.

Photochemistry of nucleic acid bases is relevant for an understanding of DNA damage by UV irradiation and cellular repair mechanisms. Absorption spectra, tautomeric equilibria, and excited state geometries of adenine [356] and cytosine [357] have been reported. A comprehensive study on absorption properties of DNA bases has appeared recently [358]. The thermochemistry of thymine dimer formation and photoinduced cycloreversion reactions occurring in DNA repair mechanisms have been investigated by Durbeej and Eriksson [359, 360]. TDDFT calculations on complexes of thymine with psoralene have

been performed to clarify the effect of psoralenes which are utilized in photochemotherapy [361].

TDDFT calculations allow to go beyond model compounds and investigate larger fragments of biological systems like the photoactive centers of green fluorescent protein [362] or photoactive yellow protein [363]. Future improvements of TDDFT such as a better description of solvation effects or QM/MM coupling may help to provide deeper insight into photochemical processes in living organisms.

6. OUTLOOK

Many phenomena in photochemistry are still not well understood, even in small model systems. The enormous complexity of photochemical processes will require a combined effort of theory and experiment to extend the frontier of our knowledge to real systems of technical and biological interest. It is clear by now that TDDFT has the potential to play an important role in this development, besides more accurate methods and experimental techniques. Nevertheless, contemporary TDDFT is *not* a black box method, and every user of commercial TDDFT codes should be aware of its limitations.

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