Nonlinear-response properties in a simplified time-dependent density functional theory (sTD-DFT) framework: Evaluation of excited-state absorption spectra

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ABSTRACT

The energy conversion efficiency of organic solar cells seems crucial for a clean future. The design of new light-harvesting devices needs an in-depth understanding of their optical properties, including the excited-state absorption (ESA). In biology, the optical characterization of photochemical/physical processes happening in photosynthetic pigments and proteins can be difficult to interpret due to their structural complexities. Experimentally, an ultrafast transient absorption experiment can probe the excited state interaction with light. Quantum chemistry could play an important role to model the transient absorption spectrum of excited states. However, systems that need to be investigated can be way too large for existent software implementations. In this contribution, we present the first sTDA/sTD-DFT (simplified time-dependent density functional theory with and without Tamm Dancoff approximation) implementation to evaluate the ESA of molecules. The ultrafast ESA evaluation presents a negligible extra cost with respect to sTDA/sTD-DFT original schemes for standard ground state absorption. The sTD-DFT method shows ability to assign ESA spectra to the correct excited state. We showed that in the literature, wrong assignments were proposed as for the L34/L44 mixture and N-methylfulleropyrrolidine. In addition, sTDA/sTD-DFT-xTB tight-binding variants are also available, allowing the evaluation of ESA for systems of a few thousands of atoms, e.g., the spectrum of the photoactive yellow protein composed of 1931 atoms.

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I. INTRODUCTION

One of the most important challenges of this century is the energetic question that raises, more and more, everyday. Organic solar cells have already shown their potential for applications like for building integrated photovoltaic devices. While the energy conversion efficiency of these solar cells is crucial for a clean future, the design of new light-harvesting devices needs an in-depth understanding of their optical properties. For this, a fundamental picture of light-matter interactions in both the chromophore ground and excited states is necessary. Experimentally, an ultrafast transient absorption experiment¹⁻⁴ can probe the excited state interaction with light. Note that the sensitivity of these pump-probe experiments is now so high that it is used as a standard method for

the detection of elementary loss channel in working organic solar cells.5-7

In biology, electron transfer processes happening in photosynthesis to avoid energy loss from internal conversion, intersystem crossing, and fluorescence are extremely fast, from 10 fs to a few nanoseconds.² Only ultrafast transient spectroscopy can probe the energy migration between systems, the formation of new chemical species, and charge-transfer states. The theoretical characterization of photochemical and photophysical processes happening in photosynthetic pigments and proteins is challenging due to the extreme complexity of structures involved.

In a transient absorption experiment, a pump laser beams the sample where 0.1%-10% of it is promoted to an excited state. After a short time delay, a weak probe laser beams the sample again and is



collected by using a multichannel detector. The transient spectrum so obtained is the difference of absorption between the pumped and the unpumped sample with the same time delay. The spectrum can be decomposed in three contributions: the ground state bleach, the stimulated emission, and the excited-state absorption (ESA). The first two contributions are of negative sign, and the third one is positive. The interpretation of such spectra can be difficult if these contributions occur in the same energy window. Beside that, the assignment of the excited states involved can also be difficult without any a priori knowledge. Usually, extra experiments need to be conducted to gather information about the assignment. In this context, quantum chemistry should play an important role to model the transient absorption spectrum of well-defined excited states. Although, systems that need to be investigated seem way too large. For example, in solar cell applications, there is real interest to use carbon dots that show structural and electronic properties very different than other nanoparticle families.^{8,9} The fundamental understanding of their photophysical properties is still under discussion, and despite their excellent optical properties, they have not performed as well as non-carbon based quantum dot solar cells, most likely because of the lack of understanding of their excited states properties.¹⁰ Carbon dots are very large systems, which cannot be treated easily by usual quantum chemistry methods. Another example is the characterization by ultrafast spectroscopy⁴ of the photoactivation mechanism in flavin-binding photoreceptors where the protein environment tunes in fine the photochemical reaction. Here also, the system size limits the theoretical characterization.

Among available quantum chemistry methods, the timedependent density functional theory (TD-DFT)¹¹⁻¹⁴ is by far the most accessible one for medium-sized systems, at least to describe the ground state absorption. Grimme and co-workers¹⁵⁻¹⁷ proposed a way to extend this level of theory to large systems by approximating two-electron integrals using short-range damped Coulomb interactions of transition density monopoles. This method is called sTD-DFT (simplified TD-DFT). A sTDA variant also exists and employs the Tamm Dancoff approximation. To treat even larger systems, it was extended to a tight-binding version with two variants called sTD-DFT-xTB and sTDA-xTB.¹⁷ The excited state absorption (ESA) of a molecule is by far more complicated to calculate since one needs to compute the double residue of the TD-DFT quadratic response.¹⁸⁻²⁴ Considering the few implementations available, ESA spectra are far to be routinely calculated.²⁵ Note that a known issue is that unphysical oscillator strengths can be computed in double resonance condition.²⁶

In this contribution, we extend the simplified scheme proposed by Grimme and co-workers^{15–17} to the ultrafast evaluation of ESA spectra. This is based on previous work where we have properly defined the quadratic-response function in the sTD-DFT framework.²⁷ Like for the evaluation of the first hyperpolarizability,²⁷ this formalism also benefits from the tight-binding versions sTD-DFTxTB and sTDA-xTB¹⁷ that allows to treat systems of a few thousands of atoms in a computationally efficient manner. While the sTD-DFT formalism is described in Sec. II, five case studies are investigated. The first one considers two 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) dyes: H₂TPyP and Ni(n)TPyP, for which Bowman *et al.*²⁸ provided reference TD-DFT calculations. The four other case studies are direct comparison with experiment: 4-propyl 4'-butyl diphenyl acetylene (L34) and its by-product 4,4-diphenylbutadiyne (L44) in a THF solution,²⁹ N-methylfulleropyrrolidine³⁰ in toluene, *s-cis-β*-carotene,³¹ and the photoactive yellow protein (PYP)³² in 10 mM Tris-HCl buffer solution at pH 8.1. With 1931 atoms, PYP is the largest system considered in this publication. Section III gives details about systems and calculations, Sec. IV presents the results, and conclusions are outlined in Sec. V.

II. THEORY

To evaluate the excited-state absorption at both sTD-DFT and sTDA levels of theory, excited state energy differences as well as state-to-state transition dipole moments need to be calculated. The state-to-state transition dipole moment is easily derived from the double residue of the TD-DFT quadratic-response function.¹⁸ We showed earlier how to evaluate the first hyperpolarizability in the sTD-DFT framework.²⁷ The formulation employed the density-matrix-based TD-DFT formalism, 11,14,19,21-24 following the derivation from Zahariev and Gordon²³ and applying the sTD-DFT approximations.^{15-17,27} In this section, we briefly recall expressions for the sTD-DFT linear- and quadratic-response functions as well as the derivation of the state-to-state transition dipole moment in both sTD-DFT and sTDA frameworks. In the following, p, q, r, s indices refer to general molecular orbitals, i, j, k, l refer to occupied, and a, b, c, d refer to unoccupied molecular orbitals.

In the density-matrix based linear-response TD-DFT formalism,^{11,14,19,21-24} the linear-response matrix equation reads

$$\begin{bmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{bmatrix} \begin{pmatrix} \mathbf{X}_{\zeta}(\omega) \\ \mathbf{Y}_{\zeta}(\omega) \end{pmatrix} = - \begin{pmatrix} \mu_{\zeta} \\ \mu_{\zeta} \end{pmatrix},$$
(1)

where $X_{\zeta}(\omega)$ and $Y_{\zeta}(\omega)$ are the frequency-dependent linearresponse vectors, $\mu_{\zeta,ai} = \langle \varphi_a | \hat{\mu}_{\zeta} | \varphi_i \rangle$,

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia|jb) - a_x(ij|ab) + (1 - a_x)(ia|f_{XC}|jb),$$
(2)
and

$$B_{ia,jb} = 2(ia|bj) - a_x(ib|aj) + (1 - a_x)(ia|f_{XC}|bj),$$
(3)

considering a global hybrid density functional in the singlet restricted case. a_x is the amount of Fock exchange, ϵ_p is the energy of the *p* orbital, (ia|jb), (ia|bj), and (ib|aj) are exchange type integrals in the Mulliken notation, (ij|ab) is a Coulomb-type integral, and $(ia|f_{XC}|jb)$ and $(ia|f_{XC}|bj)$ are the responses of the exchange-correlation functional. By switching off the time-dependent perturbation, the TD-DFT eigenvalue equation to determine excited-state energies (ω_n) and their eigenvectors $(\mathbf{X}_n$ and $\mathbf{Y}_n)$ is recovered,

$$\begin{bmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = 0.$$
(4)

Equation (4) can be simplified by assuming the popular Tamm-Dancoff approximation where the **B** matrix is neglected, leading to a Hermitian eigenvalue equation,

$$\mathbf{A}\mathbf{X} = \boldsymbol{\omega}\mathbf{X}.$$
 (5)

In the sTD-DFT framework, both **A** and **B** matrices in Eqs. (1) and (4) are simplified by neglecting the response of the exchangecorrelation functional in (2) and (3) and by approximating the Coulomb and exchange integrals by short-range damped Coulomb interactions of transition density monopoles. The two-electron approximated integrals read

$$(pq|rs)' = \sum_{A}^{N} \sum_{B}^{N} q_{pq}^{A} q_{rs}^{B} \Gamma_{AB}, \qquad (6)$$

where q_{pq}^A are transition charge densities centered on atom A determined by a Löwdin population analysis. Γ_{AB} is the Mataga-Nishimoto-Ohno-Klopman (MNOK)³³⁻³⁵ damped Coulomb operator. For Coulomb integrals $(ij|ab)'_J$, the MNOK operator takes the form

$$\Gamma_{AB}^{J} = \left(\frac{1}{(R_{AB})^{y_{f}} + (a_{x}\eta)^{-y_{f}}}\right)^{\frac{1}{y_{f}}},\tag{7}$$

where R_{AB} is the interatomic distance, y_I is a parameter, and η is the chemical hardness mean of atoms *A* and *B*. The MNOK operator is slightly different for approximated exchange integrals $(ia|jb)'_K$

$$\Gamma_{AB}^{K} = \left(\frac{1}{(R_{AB})^{y_{K}} + \eta^{-y_{K}}}\right)^{\frac{1}{y_{K}}},$$
(8)

where y_K is another parameter. Simple linear relations determine y_J and y_K parameters in the a_x range from 0 to 1.¹⁵ The chemical hardness values used are tabulated for all elements.³⁶ The simplified **A** and **B** matrix elements are expressed as

$$A'_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia|jb)'_K - (ij|ab)'_J, \tag{9}$$

$$B'_{ia,jb} = 2(ia|bj)'_{K} - a_{x}(ib|aj)'_{K}.$$
(10)

In addition to these two approximations, the CI space is truncated considering a single energy cut-off parameter.¹⁵

In this context, we recently derived the sTD-DFT quadratic-response function expression to evaluate the first hyperpolarizability, 27

$$\beta_{\xi\zeta\eta}(-(\omega_b+\omega_c);\omega_b,\omega_c)=A-B, \qquad (11)$$

$$A = \sum_{perm.\xi,\zeta,\eta} \left\{ \sum_{aij} X_{\xi,ai} (-(\omega_b + \omega_c); \omega_b, \omega_c) [-\mu_{\zeta,ij}] Y_{\eta,aj}(\omega_c) \right\}, \quad (12)$$

$$B = \sum_{perm,\xi,\zeta,\eta} \left\{ \sum_{iab} X_{\xi,ai} (-(\omega_b + \omega_c); \omega_b, \omega_c) [-\mu_{\zeta,ab}] Y_{\eta,bi}(\omega_c) \right\}, \quad (13)$$

where "*perm.* ξ , ζ , η " is related to the inclusion of six permutations of indices (and related frequencies) into the summation. Note that this expression evaluates only the unrelaxed first hyperpolarizability since we neglect both Hartree exchange-correlation and quadratic-response of the exchange-correlation functional kernels.

At both the poles $\omega_b = \omega_m$ and $\omega_c = \omega_n$ of the quadratic response function, the expectation value of the fluctuation operator $\langle m | \mu_{\xi} - \langle 0 | \mu_{\xi} | 0 \rangle | n \rangle$ that corresponds to state-to-state transition dipole moment for its non-diagonal components can be extracted from the double residue of the quadratic-response function,¹⁸

$$\lim_{\omega_{b} \to -\omega_{m}} \lim_{\omega_{c} \to \omega_{n}} (\omega_{b} + \omega_{m}) (\omega_{c} - \omega_{n}) \beta_{\xi \zeta \eta} (-(\omega_{b} + \omega_{c}); \omega_{b}, \omega_{c})$$
$$= -\langle 0 | \mu_{\zeta} | m \rangle \langle m | \mu_{\xi} - \langle 0 | \mu_{\xi} | 0 \rangle | n \rangle \langle n | \mu_{\eta} | 0 \rangle.$$
(14)

Considering that the transition dipole moment from the ground state to an excited state *m* reads

$$\langle 0|\mu_{\zeta}|m\rangle = \sqrt{2} \sum_{ia} \mu_{ia,\zeta} (X_{ia}^m + Y_{ia}^m),$$
 (15)

and that the spectral representations of the linear response vectors are expressed as

$$X_{\zeta,ai}(\omega) = \sum_{n} \mu_{ia,\zeta} \left(X_{ia}^{n} + Y_{ia}^{n} \right) \left[\frac{X_{ia}^{n}}{\omega - \omega_{n}} - \frac{Y_{ia}^{n}}{\omega + \omega_{n}} \right], \quad (16)$$

$$Y_{\zeta,ai}(\omega) = \sum_{n} \mu_{ia,\zeta} \left(X_{ia}^{n} + Y_{ia}^{n} \right) \left[\frac{Y_{ia}^{n}}{\omega - \omega_{n}} - \frac{X_{ia}^{n}}{\omega + \omega_{n}} \right], \quad (17)$$

the unrelaxed singlet-state-to-singlet-state transition dipole moment is evaluated from the double-residue of Eq. (11),

$$\left\langle m | \mu_{\xi} - \left\langle 0 | \mu_{\xi} | 0 \right\rangle | n \right\rangle = \frac{1}{2} \left\{ \sum_{aij} \left[X_{ia}^{n} \mu_{ij,\xi} X_{ja}^{m} + Y_{ia}^{m} \mu_{ij,\xi} Y_{ja}^{n} \right] - \sum_{abi} \left[X_{ia}^{n} \mu_{ab,\xi} X_{bi}^{m} + Y_{ia}^{m} \mu_{ab,\xi} Y_{bi}^{n} \right] \right\},$$
(18)

where only excited-state transition amplitudes are needed to evaluate this property. Thus, this evaluation is inexpensive after the excited-state calculation since no response vectors need to be calculated. Equation (18) can be further simplified by applying the Tamm-Dancoff approximation,

$$\left\langle m|\mu_{\xi} - \left\langle 0|\mu_{\xi}|0\right\rangle|n\right\rangle_{TDA} = \frac{1}{2} \left\{ \sum_{aij} \left[X_{ia}^{n}\mu_{ij,\xi}X_{ja}^{m} \right] - \sum_{abi} \left[X_{ia}^{n}\mu_{ab,\xi}X_{bi}^{m} \right] \right\},\tag{19}$$

where only excitation vectors \mathbf{X}_n are obtained by the sTDA procedure. The state-to-state oscillator strength

$$f_{mn} = \frac{2}{3} (\omega_m - \omega_n) \vec{\mu}_{mn} \cdot \vec{\mu}_{nm}$$
(20)

allows one to compute excited-state absorption spectra in the dipolelength formalism.

Note that the quadratic response theory presents unphysical divergences when the energy difference between two excited states matches another excitation energy. In 2016, Parker, Roy, and Furche²⁶ proposed several ways to circumvent this. Among them, they proposed to compute ESA using the "unrelaxed approximation" that ignores the relaxation of the density matrix in response to the perturbation but reproduces the correct pole structure. Our sTD-DFT/TDA formalism is developed in this "unrelaxed approximation" since we neglect both Hartree exchange-correlation and quadratic-response of the exchange-correlation functional kernels. Parker, Rappoport, and Furche show that unrelaxed transition properties tend to be overestimated but correct this unphysical behavior.²⁴

Both sTD-DFT and sTDA schemes are also interfaced with the xTB (extended basis set tight-binding) method where Kohn-Sham(KS)-DFT orbitals and energies are replaced by their xTB counterparts. This provides an unprecedented ultra-fast approach to compute excited-state absorption of large systems. The sTDA-xTB

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method is particularly important for large systems where instability can arise in the sTD-DFT-xTB scheme. This is related to the way that TD-DFT Eq. (4) is usually solved,

$$(\mathbf{A} - \mathbf{B})^{\frac{1}{2}} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{\frac{1}{2}} \mathbf{Z} = \omega^2 \mathbf{Z}, \qquad (21)$$

with

$$\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}} (\mathbf{X} + \mathbf{Y}).$$
(22)

For large systems, the xTB ground state can be unstable because of near degeneracy between the ground state and excited states. If the xTB computed ground state is close to degeneracy with another state but very slightly higher in energy, the lowest eigenvalue of (A - B) shall be negative and the evaluation of $(A - B)^{\frac{1}{2}}$ is impossible. In that case, the only alternative is the sTDA-xTB method, where the **B** matrix is neglected.

III. COMPUTATIONAL DETAILS

The sTD-DFT and sTDA methods to evaluate state-to-state transition dipole moments are implemented in the sTDA program¹⁵ for both restricted and unrestricted cases, allowing to compute singlet-to-singlet and triplet-to-triplet excited-state transitions. Since no additional solutions of linear-response equations are required to evaluate unrelaxed moments, the extra-computational time is negligible with respect to the full procedure that computes sTD-DFT or sTDA eigenvectors and excited-state energies. Thus, for a discussion about computation times, the interested reader should consult the original sTDA and sTD-DFT publications.¹⁵⁻¹⁷

We tested our implementation on five challenging cases. The first one considers two 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) dyes (Fig. 1): H₂TPyP and Ni(II)TPyP, compounds known for their optical power limiting properties. Bowman *et al.*²⁸ determined the first singlet excited-state absorption of these two dyes using quadratic-response functions with BHandHLYP and B3LYP exchange-correlation functionals. The cc-pVDZ Dunning basis set was used for H₂TPyP and 6-31G(d) Pople basis set for Ni(II)TPyP. Note that Bowman *et al.*²⁸ only provided oscillator strengths higher than 0.01. By making comparisons to their reference excited-state energies and oscillator strengths, we challenge our implementation at both sTD-DFT and sTDA levels of theory.

The second case study concerns the excite-state absorption of 4-propyl 4'-butyl diphenyl acetylene (L34) and its by-product 4,4diphenylbutadiyne (L44) in a THF solution (Fig. 1). In their experiment, Khoo *et al.*²⁹ excited the sample with a pump laser at 266 nm and 355 nm and recorded transient excited-state absorption spectra. The spectrum at 266 nm was attributed to the first singlet excited state of L34, and the one at 355 nm to the first triplet excited states of L44. Some excited-state calculations were also provided to justify their assignments including TD-DFT ones directly comparable to the experiments but where the exchange-correlation functional and basis set are not properly defined. To verify this, we optimized the L34 and L44 geometries at the PBE0/6-311G(d) level of theory and characterized the excited-state absorption with the sTD-DFT/ ω B97X-D3/6-311+G(d,p) method. Note that solvent effects are not accounted for.



1st case study: two 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) dyes: H₂TPyP and Ni(II)TPyP





3rd case study: N-methylfulleropyrrolidine

2nd case study: 4-propyl 4'-butyl diphenyl acetylene (L34) and 4,4-diphenylbutadiyne (L44)





The third case study concerns a fullerene derivative: *N*-methylfulleropyrrolidine (Fig. 1). Guldi and Prato³⁰ provided its transient singlet and triplet excited-state spectra following a picosecond flash photolysis at 355 nm, in an oxygen-free toluene solution. Like for the previous case, we will verify their assignments by following the same protocol.

The fourth case study is related to the interpretation of transient absorption spectra recorded after 60 and 300 fs following a 498 nm actinic excitation of *s*-*cis*- β -carotene (Fig. 1) in *n*-hexane recorded by Quick *et al.*³¹ The negative part of both spectra that one can observe in Fig. 2 of Ref. 31 which is due to the ground state photobleaching and the stimulated emission is not discussed here and does not impact the ESA bands. The same protocol was followed as for the two previous cases.

The last case study treats the transient ESA spectrum of the photoactive yellow protein (PYP)³⁷ (Fig. 1), a challenging case for ESA calculations usually limited to small molecules. PYP is a bluelight photoreceptor with a chromophore composed of a deprotonated *trans-p*-hydroxycinnamic acid covalently bonded to the protein by a thioester link. Changenet-Barret *et al.*³² recorded the transient ESA spectrum, 1.5 ps after a 370 nm actinic excitation. PYP is composed of 1931 atoms, too large to be treated by DFT. The optimized PYP structure was taken from Ref. 38 where it was used to calculate its circular dichroism spectrum at the sTDA-xTB level of theory. We used the sTDA-xTB method to compute its ESA spectrum and compare it to the experiment. Solvent effects are included by the implicit GBSA (generalized Born and surface area continuum solvation) model for water.³⁹

All the optimizations and SCF calculations were performed with Q-Chem 5.1⁴⁰ quantum chemistry package. The ESA calculations were computed by the sTDA program.¹⁵ For all the ESA calculations except for PYP, all excitations up to 7 eV were computed. For PYP, we increased this threshold to 9 eV. To model the ESA spectra, transition strengths were broadened by Gaussians with half width at 1/*e* maximum of 0.20 eV, except for *s*-*cis*- β -carotene where we used a value of 0.15 eV as the damping factor.

IV. RESULTS

Before discussing the five case studies, we provide a small benchmark for the ESA of five small π -conjugated molecules: trans-butadiene, phenol, naphthalene, adenine, and caffeine at the TD-DFT, sTD-DFT, and sTDA levels of theory (BHandHLYP/ccpVDZ). The TD-DFT ESA calculations were performed with DALTON2016.2^{41,42}. Table I presents singlet state-to-state excitation energies and oscillator strengths for the first $S_1 \rightarrow S_n$ dipoleallowed transition of each molecule. This comparison shows that TD-DFT oscillator strengths are well reproduced by the sTD-DFT method. Note that the sTDA method is not able to give a non-zero oscillator strength for the $S_1 \rightarrow S_5$ transition of naphthalene. The accuracy for transition energies between excited states is similar as for computing the ground state to the excited state since it uses the same excited state energies determined by the sTDA/sTD-DFT procedure. More information about this can be gathered in Refs. 15 and 16. The good agreement on this small set seems promising. Since the purpose of these methods is to treat large systems, we assessed their performance in typical applications on larger molecules.

A. Tetrapyridyl porphyrins: H₂TPyP and Ni(II)TPyP

Figure 2 presents the comparison between reference calculations from Bowman *et al.*²⁸ and sTD-DFT/TDA ones. Considering

the H₂TPyP molecule at the BHandHLYP/cc-pVDZ level of theory, only a narrow energy range is displayed in the first panel of Fig. 2 (from 2.3 to 2.7 eV) where four transitions with oscillator strengths larger than 0.01 were reported by Bowman et al.²⁸ The sTDA method reproduces the two first oscillator strengths well with less than 6.6% difference and their excitation energies with less than a 0.3% overestimation. At the sTD-DFT level, both oscillator strength and state-to-state transition energy are slightly overestimated. Using B3LYP exchange-correlation functional, only one TD-DFT value at 1.597 eV was reported by Bowman et al.²⁸ with an oscillator strength of 0.030. While the transition energy is only vaguely underestimated, the sTD-DFT and sTDA methods overestimate the oscillator strength by at least 100%. Adjusting y_I and y_K parameters for this system can probably decrease this effect. Obviously, no conclusion can be drawn from one unique transition. For Ni(II) tetrapyridyl porphyrin, the overall agreement seems good for both exchange-correlation functionals. As expected from unrelaxed calculations, the oscillator strengths are mostly overestimated by both sTDA and sTD-DFT methods and excitation energies are only slightly off. This comparison with quadratic-response function TD-DFT calculations is promising as for the smaller molecules. Direct confrontations to the experiment can provide further assessments.

B. 4-Propyl 4'-butyl diphenyl acetylene (L34) and its by-product 4,4-diphenylbutadiyne (L44)

Figure 3 presents the experimental transient ESA spectra recorded using pump wavelengths of 266 nm and 355 nm for L34/L44 mixture in THF.²⁹ In their study, Khoo et al.²⁹ assigned the spectrum recorded at a pump wavelength of 355 nm to the triplet state of L44 and the one at a pump wavelength of 266 nm to the third singlet state of L34. This was supposedly justified by excitedstate energy calculations performed at the TD-DFT level but without providing the usual exchange-correlation functional and basis set information. Thus, we are unable to estimate the validity of this justification, at least, before running any calculations. To verify these assessments, the ESA spectra were computed for both first singlet and triplet states of L34 and L44 at the sTD-DFT/wB97X-D3/6-311+G(d,p) level of theory. Note that we have not computed higher energy singlet ESA spectra because they are out of reach of these pump excitations. The comparison with respect to the experiment is provided in Fig. 3 and is straightforward confirming their findings

TABLE I. Singlet-to-singlet excited state absorption energies and oscillator strengths for five small π -conjugated molecules at the TD-DFT, sTD-DFT, and sTDA levels of theory (BHandHLYP/cc-pVDZ).

		TD-DFT		sTD-DFT		sTDA	
	Transition $m \rightarrow n$	E _{mn} (eV)	f _{mn}	E _{mn} (eV)	f _{mn}	E _{mn} (eV)	f_{mn}
trans-butadiene	$S_1 \rightarrow S_5$	1.936	0.102	1.631	0.104	1.330	0.087
Phenol	$S_1 \rightarrow S_6$	1.967	0.003	2.008	0.004	2.287	0.007
Naphthalene	$S_1 \rightarrow S_5$	1.880	0.089	1.753	0.137	1.952	0.000
Adenine	$S_1 \rightarrow S_8$	1.617	0.080	1.611	0.061	1.582	0.012
Caffeine	$S_1 \rightarrow S_3$	1.206	0.005	1.245	0.003	1.150	0.003



FIG. 2. First singlet excited-state to excited-state oscillator strengths of H₂TPyP and Ni(II)TPyP at the TD-DFT level from Bowman *et al.*²⁸ compared to sTD-DFT and sTDA ones. Both B3LYP and BHandHLYP exchange-correlation functionals are considered. The cc-pVDZ basis set is used for H₂TPyP, and the cc-pvDZ one for Ni(II)TPyP.

for the spectrum recorded at a pump wavelength of 355 nm that corresponds to the triplet state ESA of L44 where a small energy shift is observed. Note again that solvent effects are not accounted for. But for the spectrum at a pump wavelength of 266 nm, it should be attributed to the ESA of the first triplet state of L34 instead to any singlet excited state, as it was suggested by Khoo *et al.*²⁹ Both experimental peaks are reproduced by the calculation, but the band around 3.9 eV has a smaller intensity than the experimental one.



FIG. 3. Transient excited-state absorption spectra obtained with 266 nm and 355 nm laser excitations of L34 and its by-product L44 in a THF solution²⁹ compared to sTD-DFT/ ω B97X-D3/6-311+G(d,p) calculations for their first triplet and singlet excited-state absorption spectra.

The second peak has a similar magnitude with respect to the experiment but is slightly shifted, like for the L44 comparison. Note that the triplet ESA sTD-DFT calculation of L44 was the longest computation on this study case with 0.14 min on an eight-core desktop computer (Intel core i7-6700, 3.40 GHz).

C. N-methylfulleropyrrolidine

Figure 4 presents the transient ESA spectra of N-methylfulleropyrrolidine in toluene following a picosecond flash photolysis at 355 nm, recorded by Guldi and Prato.³⁰ Two spectra were recorded following the supposed mechanism that the C₆₀ derivative is first excited to the first singlet excited state and shortly after decays to the first triplet excited state that has a quite longer lifetime. Our first guess was to compute the first singlet and first triplet excited states of N-methylfulleropyrrolidine, but the triplet ESA spectrum we obtained showed noticeable ESA only between 4 and 6 eV, out of the range of the spectra measured by Guldi and Prato. The second observation is that the spectrum they assigned to the triplet state is matching very well our sTD-DFT first singlet ESA spectrum with a shift of -1.0 eV, as one can see in Fig. 4. We computed the second singlet ESA and found that it is also well matching the shape of the spectra supposedly assigned to the first singlet state (Fig. 4) with the same -1.0 eV of energy shift. In conclusion, we propose that the excitation mechanism is more likely to be that the C₆₀ derivative is first excited to the second singlet excited state and decays to the first singlet excited state. Note that all sTD-DFT calculations took less than a minute on an eight-core desktop computer (Intel core i7-6700, 3.40 GHz).

D. *s*-*cis*- β -carotene

Figure 5 presents transient ESA spectra of *s*-*cis*- β -carotene³¹ in *n*-hexane following a 498 nm pump excitation recorded after 60



FIG. 4. Transient ESA spectra of N-methylfulleropyrrolidine³⁰ in toluene following a picosecond flash photolysis at 355 nm, attributed to the first singlet excited state and the first triplet excited state compared to sTD-DFT/ ω B97X-D3/6-311+G(d,p) calculations for the first and second singlet excited-state absorption spectra shifted by -1.0 eV.

and 300 fs. After 60 fs, *s*-*cis*- β -carotene is still excited in its second singlet excited state. This is corroborated by our sTD-DFT/ ω B97X-D3/6-311+G(d,p) ESA spectrum presented in Fig. 5 where a small



FIG. 5. Transient ESA spectra of *s*-*cis*- β -carotene³¹ in *n*-hexane following a 498 nm pump excitation recorded after 60 and 300 fs compared to sTD-DFT/ ω B97X-D3/6-311+G(d,p) calculations for their first and second singlet excited-state absorption spectra.

shift of 0.4 eV is observed with respect to the experiment. After 300 fs, the *s*-*cis*- β -carotene solution has decayed to the first singlet excited state. This is also in agreement with our calculated spectrum considering the same energy shift (see Fig. 5). Note that the small shoulder observed in the experiment around 1.2 eV is probably due to a small amount of molecules still excited in the S₂ state. Both ESA calculations took about 6 s on an eight-core desktop computer (Intel core i7-6700, 3.40 GHz). As an intermediate conclusion following these three last case studies, the sTD-DFT approach to compute ESA seems to be well suited to assign experimental ESA spectra at very low computational cost.

E. Photoactive yellow protein

Figure 6 presents the transient absorption of PYP³² in a 10 mM Tris-HCl buffer solution at pH 8.1, 1.5 ps after a 370 nm pump excitation. While for the previous study cases, spectra were not impacted by the ground state bleaching and the stimulated emission, for PYP, the spectrum is mostly of negative sign due to those effects. Three bands are present: around 370 nm an ESA, at 445 nm the ground state bleaching, and at 495 nm the stimulated emission. To model this, we have calculated the ground state absorption and the first singlet ESA with the sTDA-xTD semi-empirical approach. To represent the stimulated emission, the modeled Gaussian absorption was shifted to higher wavelengths by 70 nm. Note that both ground state absorption and stimulated emission bands are inhomogeneously broadened as it can be seen in Fig. 1 of Ref. 32. Modeling vibronic structures of such large system is obviously out of the scope of this article. A global energy shift of -0.5 eV was applied to match the experiment. To reproduce the experimental transient absorption spectrum, we subtracted from the ESA, the ground state absorption



FIG. 6. Transient absorption of PYP³² in a 10 mM *Tris*-HCl buffer solution at pH 8.1, 1.5 ps after a 370 nm actinic excitation, compared to sTDA-xTB first singlet excitation, absorption, "fake" stimulated emission, and the simulated transient spectra.

and the "fake" stimulated emission spectra (see Fig. 6). The result is qualitatively in good agreement with respect to the experiment and allows one to explain the transient spectrum main features. The experimental ESA band around 370 nm is not well reproduced by the sTDA-xTB ESA band around 410 nm for which the strength is underestimated. The calculated transient spectrum shows well how the stimulated emission band is attenuated by the ESA. However, the shape of this band is not perfect. This is mainly due to the absence of the vibronic structure in the "fake" stimulated emission band and probably to a too broad ESA band. The comparison is not perfect but allows one to explain the main features of this transient spectrum. The calculation of the ESA spectrum by the sTDA program took less than 2 h on a 28-cpu computer node. The evaluation of the ESA by the sTDA-xTB method opens the way to a broad range of applications like in photobiology where the characterization of transient ESA by ultrafast spectroscopy is widely used to understand photochemical processes.

V. CONCLUSIONS AND OUTLOOKS

In this article, we have presented the first sTDA/sTD-DFT implementation to evaluate the excited-state absorption of molecules in an unrelaxed fashion. To calculate the excited states and their energies, the simplified theory approximates the TD-DFT approach by approximating the two-electron integrals, neglecting the exchange-correlation response, and truncating the CI space. Since no extra linear-response vectors need to be computed, the ESA evaluation presents a negligible extra cost with respect to sTDA/sTD-DFT original schemes. In addition, sTDA/sTD-DFTxTB tight-binding variants are also available, allowing the evaluation of ESA for systems of a few thousands of atoms for the first time. While ultrafast for medium-sized systems, the sTD-DFT method shows ability to assign ESA spectra to the correct excited state. From an experimental point of view, these assignments are not easy and usually need extra experiments. We showed that in the literature, wrong assignments are present as for the L34/L44 mixture and Nmethylfulleropyrrolidine. In an hour of work, where the geometry optimization takes most of the time, a theoretical assignment can be proposed. The sTDA-xTB tight-binding method was able to determine the ESA spectrum of the photoactive yellow protein composed of 1931 atoms and to explain main features of the transient spectrum. This opens the way to a better understanding of photochemical and photophysical processes present in biology and for the design of new efficient organic solar cells where ESA spectra need to be clearly identified.

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