Accurate Relativistic Real-Time TDDFT for Valence and Core Attosecond Transient Absorption Spectroscopy

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Abstract

Attosecond pump–probe transient absorption spectroscopy (TAS) has opened the possibility to study pure electron dynamics on its natural time scale. However, due to the out-of-equilibrium nature of the process, first-principle theoretical modelling remains a challenging task, specially for heavy elements and/or core excitations where relativistic corrections become imperative, as the spectra contain significant imprints of both scalar and spin-orbit relativistic effects. To alleviate this problem, we formulated a methodology for computing TAS spectrum within the relativistic real-time time-dependent density functional theory (RT-TDDFT) framework, for both the valence and core energy regime. Even though RT simulations using full four-component (4c) method are feasible, they are still computationally expensive, especially for TAS. Therefore, in addition to the 4c approach, we have introduced the atomic mean-field exact two-component (amfX2C) Hamiltonian for RT-TDDFT, which accounts for one- and two-electron picture-change corrections and preserves the accuracy of the parent 4c method but at a fraction of its computational cost. Finally, we apply the amfX2C approach to study valence and near L_{2,3}-edge TAS processes of experimentally relevant systems, providing additional physical insights through the lens of non-equilibrium response theory.

Graphical TOC Entry
Transient absorption spectroscopy (TAS) is a powerful non-linear technique for investigating ultrafast state-resolved processes and electronic superposition using two pulses, \textit{viz} pump and time-delayed probe pulse.\textsuperscript{1-3} TAS offers additional degrees of freedom, namely, pump field features like shape, amplitude, carrier frequency, direction, and pump-probe time delays, absent in conventional spectroscopy. Of which, the effect of time-delay between the pulses is most commonly followed experimentally.\textsuperscript{4,5} Since long, the emphasis has been on the femto- to pico-second timescales, which involved time-resolving processes initiated by nuclear motions.\textsuperscript{6-9} However, with the advent of atto-second pulses, there has been an ever increasing interest in studying sub-femtosecond timescale processes, focusing on the motion of electrons on their natural time-scale, with minimal influence of nuclear degrees of freedom.\textsuperscript{2,10-19} Simultaneously, generation of intense isolated soft X-ray free electron laser pulses with sub-femtosecond temporal widths has been achieved recently, promoting investigations of attosecond resolved spectroscopies involving core orbitals.\textsuperscript{20,21} Due to their characteristic element specificity and unprecedented temporal resolution, ultrafast X-ray spectroscopies are emerging as indispensable tools for biological and material sciences.\textsuperscript{22,23} Especially X-ray transient absorption spectroscopy (XTAS) which employs short X-ray probe pulses is now extensively being used to investigate electron dynamics of molecules and solid-state systems.\textsuperscript{7,22-27} This dictates the need to develop reliable theoretical tools to aid the interpretation and prediction of such phenomena.

With regards to simulating the response of the laser pulses relevant to pump-probe spectroscopies, real-time (RT) formalism offers a straightforward approach\textsuperscript{28-44} over response theory based methods as the former is applicable for a large range of field intensities, and resembles the experimental setup in a natural way. Addressing core level spectroscopies has added complexities, as it requires the inclusion of scalar (SC) and spin-orbit (SO) relativistic effects. Therefore, the extension of the RT framework\textsuperscript{45} to the relativistic regime was also formulated recently both at the four-component (4c)\textsuperscript{46-48} and two-component (2c)\textsuperscript{49-51} level.

In this letter, we present a novel theoretical methodology to address several fascinating
characteristics associated with TAS and its simulation. First, to understand the physics
governing TAS, we generalize the non-equilibrium response theory formalism to incorporate
complex orbitals necessary for relativistic theory. This facilitates us to interpret unique spec-
tral observations inherent to TAS. Next, to provide first-principle computational approach
for simulation of TAS across the entire Periodic Table and/or core atomic region(s), we
implement a relativistic variant of RT time-dependent density functional theory (TDDFT)
based on 4c Dirac–Coulomb Hamiltonian. This allows us to account for SC and SO relativis-
tic effects variationally, thereby significantly broadening the applicability of the tool. Since
the gold standard 4c method is still computationally demanding and popular one-electron
exact two-component (1eX2C) is not sufficiently accurate in comparison to its 4c analogue,
finally we formulate and implement for the first time simple yet numerically accurate atomic
mean-field exact two-component (amfX2C) Hamiltonian in context of RT framework. It
incorporates all spin-free and spin-dependent relativistic picture-change corrections origi-
nating from X2C transformation, giving remarkable agreement with reference 4c results.
Consequently, we apply the amfX2C Hamiltonian to provide physical insights into TAS near
valence and L_{2,3}-edge for experimentally relevant systems.

In order to lay the theoretical foundations for describing pump-probe spectroscopy, we
consider in this work the non-overlapping regime, in which the probe field/pulse \( \mathcal{F}(t) \) is
applied at or after the end of the pump pulse \( \mathcal{E}(t) \). The pump pulse takes the form

\[
\mathcal{E}(t) = n \mathcal{E}(t) = n \mathcal{E}_0 \cos^2 \left( \frac{t-t_0}{T} \right) \sin(\omega_0 t + \phi),
\]

and is characterized by the amplitude \( \mathcal{E}_0 \), shape (cos\(^2\)-enveloped sin function), carrier fre-
quency \( \omega_0 \), time duration \( T \), carrier–envelope phase (CEP) \( \phi \), and polarization along the
unit vector \( n \). The pump pulse is centered at \( t_0 \), and is zero (inactive) outside of the window
of size \( T \), \textit{i.e.} for \( t < t_0 - \frac{T}{2} \) and \( t > t_0 + \frac{T}{2} \). In practice, the duration of the pump is chosen
to be an integer number of carrier periods and the time \( t = 0 \) corresponds to the onset of
the pump, i.e. \( t_0 = \frac{T}{2} \), and the CEP is set to 0. For the probe pulse, we use the analytical form of a delta field

\[
F(t) = m F_0(t) = m F_0 \delta(t - (T + \tau)),
\]

characterized by its amplitude \( F_0 \), polarization direction \( m \), and positioned at \( T + \tau \), where \( \tau \) is a time-delay between pump and probe pulse.

To get physical insight into pump–probe processes, it is instructive to examine them from the point of non-equilibrium response theory. First, we derive the non-perturbative form of the response to the probe field applied to the non-stationary (out-of-equilibrium) state \( \Psi[\mathcal{E}] \) generated by the previous pump pulse lasting from time 0 to \( T \). The time evolution of a system after the end of the pump is described by the Hamiltonian,

\[
\hat{H}(t) = \hat{H}_0 - \sum_{u \in x,y,z} F_u(t) \hat{P}_u; \quad \hat{P}_u = -N \sum_{i=1}^N \hat{r}_{i,u},
\]

where \( \hat{H}_0 \) is the static Hamiltonian describing the \( N \) electron system itself, and \( \sum_{u \in x,y,z} F_u(t) \hat{P}_u \) denotes the coupling of the molecular system to the probe pulse via the electric dipole operator \( \hat{P} \). Note that we have assumed the dipole approximation and we work in the length gauge all over the paper. Using the closed form of the perturbation operator in combination with the evolution operators derived from Eq. (3), the wave function at time \( t > T + \tau \) is given by

\[
|\Psi(t)\rangle = e^{-i\hat{H}_0(t-T-\tau)} e^{-i\hat{Q}_v} e^{-i\hat{H}_0\tau} |\Psi[\mathcal{E}]\rangle,
\]

where \( \hat{Q}_v \equiv -\mathcal{F}_0 \hat{P}_v \). In the basis of stationary eigenstates \( |\Phi_j\rangle \) of the static Hamiltonian \( \hat{H}_0 \), the state \( |\Psi[\mathcal{E}]\rangle \) is expressed as a linear combination

\[
|\Psi[\mathcal{E}]\rangle = \sum_j c_j(\mathcal{E}) |\Phi_j\rangle; \quad c_j(\mathcal{E}) = \langle \Phi_j | \Psi[\mathcal{E}] \rangle.
\]

Using the resolution-of-the-identity \( \sum_j |\Phi_j\rangle \langle \Phi_j| = \hat{1} \), the non-perturbative electric dipole
response to the probe pulse $P_u[\mathcal{E}, \mathcal{F}](t) = \langle \Psi(t)|\hat{P}_u|\Psi(t)\rangle$ can be written in the frequency domain as

$$P_u[\mathcal{E}, \mathcal{F}](\omega) = i \sum_{jkm} c_j(\mathcal{E})c_k^*(\mathcal{E})e^{i\omega_{jk} \tau} \frac{P_{u,km} (e^{-iQ_v})_{jk} P_{u,km} (e^{iQ_v})_{mn}}{\omega_{km} + \omega + i\Gamma},$$

(6)

where $\omega_{jk} \equiv \epsilon_j - \epsilon_k$ is the difference between the energies of the stationary states, for an operator $\hat{A}$, $A_{jk} \equiv \langle \Phi_j|\hat{A}|\Phi_k\rangle$ is its matrix element, $P_u(\omega) = \int_{T+\tau}^{\infty} P_u(t)e^{(i\omega-\Gamma)(t-T-\tau)}dt$ and a damping parameter $\Gamma$ is introduced to regularize the Fourier integral over oscillating functions and facilitate its practical evaluation in simulations with a finite time length. Using the expansion $e^{-iQ_v} \equiv e^{i\mathcal{F}_0 P_v} = I + i\mathcal{F}_0 P_v + \ldots$ in Eq. (6) allows us to understand the most dominant effects on the resulting spectra, i.e. those that appear even in the weak probe field limit. After rearranging the summation indices, we obtain the first terms

$$P_u^{(0)}[\mathcal{E}, \mathcal{F}](\omega) = i \sum_{jk} c_j(\mathcal{E})c_k(\mathcal{E})e^{-i\omega_{jk} \tau} \frac{P_{u,kj}}{\omega - \omega_{jk} + i\Gamma},$$

(7)

and

$$\frac{P_u^{(1)}[\mathcal{E}, \mathcal{F}](\omega)}{\mathcal{F}_0} = \sum_{jkm} c_j(\mathcal{E})c_k^*(\mathcal{E})e^{-i\omega_{jk} \tau} \frac{P_{v,km} P_{u,mj}}{\omega - \omega_{jm} + i\Gamma} + \text{c.c.}(\omega \rightarrow -\omega),$$

(8)

where c.c.$(\omega \rightarrow -\omega)$ labels the complex conjugation while flipping the sign of the frequency.

We note, that in the relativistic theory presented here, the stationary wave functions are complex in general. As a consequence, the matrix elements $P_{v,km}$ can no longer be assumed to be real. Expressions in Eqs. (7) and (8) are in contrast with the equilibrium response theory where a response function is defined in terms of a specific eigenstate of $\hat{H}_0$, e.g. $|\Psi[\mathcal{E}]\rangle \equiv |\Phi_0\rangle$, and $c_j(\mathcal{E}) \equiv \delta_{j0}$ — assuming this would yield the equilibrium response functions.

The process of electronic absorption, that is of interest here, is associated with the imaginary part of the electric dipole–electric dipole response function in the frequency domain $(\chi_{\hat{P}_u,\hat{P}_v}\mathcal{E}](\omega, T + \tau) \equiv P_u^{(1)}[\mathcal{E}, \mathcal{F}](\omega)/\mathcal{F}_0).$ The resulting expression for the response function was presented by other authors, while assuming that the eigenstates $|\Phi_j\rangle$, and hence
the matrix elements $P_{v,km}$ are real-valued. However, this is not the case in the relativistic theory, and we here proceed by deriving the relativistic extension for the response function without making this assumption. Let $\phi_j$ denote the phase of the complex amplitudes $c_j$, i.e. $c_j = |c_j|e^{i\phi_j}$. By defining $\Theta_{jk}(\tau) \equiv \phi_j - \phi_k - \omega_{jk}\tau$ and using $1/(\omega + i\Gamma) = \mathcal{R}(\omega) - i\mathcal{L}(\omega)$, where $\mathcal{L}$ and $\mathcal{R}$ represent Lorentzian and Rayleigh lineshape functions, respectively, we can rearrange the terms in Eq. (8) and extract the imaginary part as

$$\Im \tilde{\chi}_{P_u,P_u}[\mathcal{E}](\omega, T + \tau) = \sum_{jkm} |c_j(\mathcal{E})c_k(\mathcal{E})|\Re (P_{v,km}P_{u,mj})$$

$$\times \left[ \sin \Theta_{jk}(\tau)\mathcal{R}(\omega - \omega_{jm}) - \cos \Theta_{jk}(\tau)\mathcal{L}(\omega - \omega_{jm}) + \sin \Theta_{jk}(\tau)\mathcal{R}(\omega + \omega_{jm}) + \cos \Theta_{jk}(\tau)\mathcal{L}(\omega + \omega_{jm}) \right]$$

$$+ \sum_{jkm} |c_j(\mathcal{E})c_k(\mathcal{E})|\Im (P_{v,km}P_{u,mj})$$

$$\times \left[ \cos \Theta_{jk}(\tau)\mathcal{R}(\omega - \omega_{jm}) + \sin \Theta_{jk}(\tau)\mathcal{L}(\omega - \omega_{jm}) - \cos \Theta_{jk}(\tau)\mathcal{R}(\omega + \omega_{jm}) - \sin \Theta_{jk}(\tau)\mathcal{L}(\omega + \omega_{jm}) \right].$$

(9)

The first part of this expression proportional to the real part $\Re (P_{v,km}P_{u,mj})$ coincides with the result of Walkenhorst et al.\textsuperscript{54} for $P_{v,km} \in \mathbb{R}$. The second part is nonzero only for the relativistic theory that requires formulation using complex orbitals. We note here, that this distinction between the nonrelativistic and relativistic theories is a unique feature of the non-equilibrium response function and does not appear when the non-stationary state $|\Psi[\mathcal{E}]\rangle$ is replaced with a single eigenstate (for spatially isotropic values $\Im \tilde{\chi}_{P_u,P_u}$). Finally, we mention that the diagonal terms $j = k$ in the sums in Eq. (9) can be isolated to study separately the time delay-independent contribution and interference term that depends on the time delay $\tau$. The interference term is a signature of the non-stationary state, leading to the spectral dependence on $\tau$. $\Theta_{jk}$ combines the real and imaginary part of the response function and interchanges the $\mathcal{L}$ to $\mathcal{R}$ lineshapes, and vice-versa. The imprints of Eq. (9) can be directly connected to the simulated spectral observations and are discussed later.
Instead of using the non-equilibrium response theory to obtain TAS spectra, we work directly in time domain and evolve a molecular system of interest by the Liouville–von Neumann equation-of-motion (EOM). For Kohn–Sham TDDFT in an orthonormal basis, EOM takes the form

\[ i \frac{\partial \mathbf{D}(t)}{\partial t} = [\mathbf{F}(t), \mathbf{D}(t)], \tag{10} \]

where \( \mathbf{D}(t) \) is the time-dependent reduced one-electron density matrix describing the state of the system at time \( t \) and \( \mathbf{F}(t) \) is the Fock matrix driving the time evolution and characterizing the molecular system itself as well as its interaction with the external pump–probe fields. In practice, Eq. (10) is solved numerically by propagating \( \mathbf{D}(t) \) in time as detailed in Ref. 31,46, 55 and 56 as well as in Section S1.

The theoretical modelling of core–level spectroscopies is a challenging task because the spectra feature a fine structure due to scalar (SC) and spin–orbit (SO) relativistic effects. 47,57–61 With this in mind, we have extended our recent probe-only four-component (4c) RT-TDDFT implementation46,47,62 to the realm of pump–probe experiments. Assuming an orthonormalized atomic orbital (AO) basis, the 4c Fock operator suitable for TAS has the following matrix form

\[
F^{4c}_{\mu\nu}(t) = F^{4c}_{\mu\nu}[\mathcal{E},\mathcal{F}](t) = h^{4c}_{\mu\nu} - \sum_{u \in x,y,z} P^{4c}_{u,\mu\nu} \mathcal{E}_u(t) - \sum_{u \in x,y,z} P^{4c}_{u,\mu\nu} \mathcal{F}_u(t) + \sum_{\kappa\lambda} G^{4c}_{\mu\nu,\kappa\lambda} D^{4c}_{\kappa\lambda}(t, \mathcal{E}, \mathcal{F}) + \sum_{u \in 0-3} \int v^{xc}_{u} [\rho^{xc}(r, t, \mathcal{E}, \mathcal{F})] \Omega^{4c}_{u,\mu\nu}(r) d^3r, \tag{11} \]

where terms on the right hand side include the one-electron Dirac operator (\( h^{4c} \)), particle-field interactions via the electric dipole moment operator (\( P^{4c}_u \)), two-electron (2e) Coulomb and exchange interactions, and the exchange–correlation (xc) contribution. Here, the 2e
term involves the matrix of generalized anti-symmetrized electron repulsion integrals

\[ C_{\mu\nu,\kappa\lambda}^{4c} = T_{\mu\nu,\kappa\lambda}^{4c} - \zeta T_{\mu\lambda,\kappa\nu}^{4c}; \quad T_{\mu\nu,\kappa\lambda}^{4c} := \int \int \Omega_{\mu,\nu}^{4c}(r_1) r_{12}^{-1} \Omega_{\kappa,\lambda}^{4c}(r_2) d^3r_1 d^3r_2, \] (12)

with a scalar scaling factor \( \zeta \) for exchange interaction, whereas the xc term requires a non-collinear xc potential \( v^{xc}_u \), given within a generalized gradient approximation (GGA) by derivatives of the nonrelativistic xc energy density \( (\varepsilon^{xc}) \) with respect to the 4c electronic charge density \( (\rho_u^{4c}) \), spin densities \( (\rho_{1-3}^{4c}) \), as well as their gradients:

\[ v^{xc}_u[\rho^{4c}] = \frac{\partial \varepsilon^{xc}}{\partial \rho_u^{4c}} - \left( \nabla \cdot \frac{\partial \varepsilon^{xc}}{\partial \nabla \rho_u^{4c}} \right), \quad \rho_u^{4c}(r, t, \mathbf{E}, \mathbf{F}) = \sum_{\mu\nu} \Omega_{u,\mu\nu}^{4c}(r) D^{4c}_{\nu\mu}(t, \mathbf{E}, \mathbf{F}). \] (13)

More details about our noncollinear extension of nonrelativistic xc potentials are available in Ref. 63. In Eqs. (12) and (13), \( \Omega_u^{4c} \) stands for the matrix of overlap distribution functions:

\[ \Omega_{u,\mu\nu}^{4c}(r) = X_{\mu}(r)^\dagger \Sigma_u X_{\nu}(r), \quad \Sigma_u = \begin{pmatrix} \sigma_u & 0_2 \\ 0_2 & \sigma_u \end{pmatrix}, \] (14)

defined as the product of orthonormal 4c AO basis functions \( X_{\mu}(r) := X_{\mu}^{RKB}(r) \) fulfilling a restricted kinetic balance (RKB) condition in their small-component, and 4c operators associated with the electronic charge density \( (\Sigma_0) \) and spin densities \( (\Sigma_{1-3}) \). The latter ones are defined via the \( 2 \times 2 \) zero matrix \( (0_2) \), identity matrix \( (\sigma_0) \), and Pauli spin matrices \( (\sigma_1, \sigma_2, \sigma_3) \). Note that prior to their use in Eq. (10), both Fock and density matrix are transformed into the basis of ground-state molecular orbitals, obtained from the solution of self-consistent field equations.

While simulations of XAS by means of full 4c RT-TDDFT method are nowadays feasible, its extension towards pump-probe experiments becomes computationally expensive. Therefore, there is interest in developing approximate relativistic methods enabling RT calculations in two-component (2c) regime while maintaining the accuracy of the parent 4c
approach. Therefore, alongside of the 4c method that serves as a gold-standard reference, we put-forth a first formulation and implementation of an atomic mean-field exact two-component Hamiltonian (amfX2C) within the realm of RT-TDDFT and apply it to simulate (X)TAS spectra. As proven for self-consistent field calculations, the simple yet numerically accurate amfX2C approach accounts for so-called SC and SO two-electron (2e) and exchange–correlation (xc) picture-change (PC) effects that arise from the X2C transformation, in contrast to the commonly used one-electron X2C (1eX2C) Hamiltonian. Furthermore, as demonstrated on simple XAS spectra of transition metal and actinide compounds, the absence of these PC effects in 1eX2C results in a substantial overestimation of L- and M-edge SO splittings, whereas the amfX2C Hamiltonian reproduces all essential spectral features such as shape, position and SO splitting in excellent agreement with 4c references, while offering significant computational savings.

The central idea of our RT-TDDFT amfX2C approach is the matrix transformation of the original 4c EOM in Eq. (10) to its diagonally-dominant form using a static (time-independent) unitary matrix $U$. By maintaining only the large-component–large-component (LL) block of the transformed 4c EOM, one arrives at the 2c EOM

$$i \frac{\partial \tilde{D}^{2c}(t)}{\partial t} = [\tilde{F}^{2c}(t), \tilde{D}^{2c}(t)]$$

with so-called 2c PC transformed Fock and density matrix

$$\tilde{F}^{2c}_{\mu\nu}(t) = \left[U^\dagger F^{4c}(t)U\right]^{LL}_{\mu\nu}, \quad \tilde{D}^{2c}_{\mu\nu}(t) = \left[UD^{4c}(t)U^\dagger\right]^{LL}_{\mu\nu}. \quad (16)$$

In consistency with our previous works we use notation with tildes to indicate picture-change transformed quantities. Of significant importance is the observation that the correctly transformed 2c Fock matrix involves not only the PC transformed density matrix ($\tilde{D}^{2c}$), but also overlap distribution matrix, as well as one- and two-electron integrals. In connection
to Eq. (11), our 2c RT-TDDFT (X)TAS reads

$$
\tilde{F}^{2c}_{\mu\nu}(t) = \tilde{F}^{2c}_{\mu\nu}[\mathcal{E}, \mathcal{F}](t) = \tilde{h}^{2c}_{\mu\nu} - \sum_{u \in x,y,z} \tilde{P}^{2c}_{u,\mu\nu} \mathcal{E}_u(t) - \sum_{u \in x,y,z} \tilde{P}^{2c}_{u,\mu\nu} \mathcal{F}_u(t)
+ \sum_{\kappa \lambda} \tilde{G}^{2c}_{\mu\nu,\kappa\lambda} \tilde{D}^{2c}_{\kappa\lambda}(t, \mathcal{E}, \mathcal{F}) + \sum_{u \in 0-3} \int v^{xc}_u \left[ \rho^{2c}(r, t, \mathcal{E}, \mathcal{F}) \right] \tilde{\Omega}^{2c}_{u,\mu\nu}(r) \, d^3r.
$$

(17)

Note however, that the presence of picture-change transformed overlap distribution matrix ($\tilde{\Omega}^{2c}$) in both 2e and xc interaction terms makes the evaluation of $\tilde{F}^{2c}$ computationally more demanding than the original 4c Fock matrix. Therefore, in line with the amfX2C approach introduced originally for the static (time-independent) SCF case\cite{65} and extended later to the response theory formalism involving electric field(s),\cite{66} $\tilde{F}^{2c}$ in Eq. (17) can be approximated by a computationally efficient form built with untransformed (without the tilde) overlap distributions ($\Omega^{2c}$), i.e.,

$$
\tilde{F}^{2c}_{\mu\nu}(t) \approx \tilde{F}^{\text{amfX2C}}_{\mu\nu}[\mathcal{E}, \mathcal{F}](t) = \tilde{h}^{2c}_{\mu\nu} - \sum_{u \in x,y,z} \tilde{P}^{2c}_{u,\mu\nu} \mathcal{E}_u(t) - \sum_{u \in x,y,z} \tilde{P}^{2c}_{u,\mu\nu} \mathcal{F}_u(t) + \Delta \tilde{F}^{\text{amfX2C}}_{\mu\nu}
+ \sum_{\kappa \lambda} \tilde{G}^{2c}_{\mu\nu,\kappa\lambda} \tilde{D}^{2c}_{\kappa\lambda}(t, \mathcal{E}, \mathcal{F}) + \sum_{u \in 0-3} \int v^{xc}_u \left[ \rho^{2c}(r, t, \mathcal{E}, \mathcal{F}) \right] \Omega^{2c}_{u,\mu\nu}(r) \, d^3r.
$$

(18)

In fact, Eq. (18) defines our 2c amfX2C Fock matrix applied in actual RT (X)TAS simulations. Here, the picture-change corrections, defined as the difference between transformed and untransformed 2e and xc interaction terms, are take into account approximately via $\Delta \tilde{F}^{\text{amfX2C}}_{\mu\nu}$ and given by a superposition of corresponding static atomic quantities:\cite{65,66}

$$
\Delta \tilde{F}^{\text{amfX2C}}_{\mu\nu} = \bigoplus_{K=1}^{M} \Delta \tilde{F}^{2c,2e}_K + \Delta \tilde{F}^{2c,xc}_K,
$$

(19)
where

\[
\Delta \tilde{F}_{K}^{2c,2c} = \left( \tilde{G}_{K}^{2c} - G_{K}^{2c} \right) \tilde{D}_{K}^{2c} \tag{20}
\]

\[
\Delta \tilde{F}_{K}^{2c,xc} = \sum_{u \in 0-3} \int v_{u}^{xc} \left[ \tilde{\rho}^{2c}_{K}(r) \right] \tilde{\Omega}_{u}^{2c}(r) d^{3}r - \sum_{u \in 0-3} \int v_{u}^{xc} \left[ \rho^{2c}(r) \right] \Omega_{u}^{2c}(r) d^{3}r. \tag{21}
\]

Here, \( K \) runs over all atoms in an \( M \)-atomic system and labels atomic quantities obtained from independent atomic SCF calculations, each performed in the orthonormal AO basis of \( K \)th atom. While a theoretical justification enabling us to build \( \Delta \tilde{F}_{\Theta}^{\text{amfX2C}} \) from static (time-independent) quantities is available in Ref. [66], a pseudo-code highlighting the essential steps for evaluating \( \Delta \tilde{F}_{\Theta}^{\text{amfX2C}} \) is presented in Ref. [65].

The final TAS spectra are obtained within the RT-TDDFT framework from the differential induced dipole moment

\[
\Delta \mu_{uv}^{\text{TAS}}(t) = \text{Tr} \left\{ P_{uv} [D_{p}^{pp}(t) - D_{p}^{p}(t)] \right\} \equiv \mu_{uv}^{\text{ind,pp}}(t) - \mu_{uv}^{\text{ind,p}}(t), \quad u, v \in \{x, y, z\}, \tag{22}
\]

where \( \mu_{uv}^{\text{ind}}(t) \) denotes the expectation value of the dipole operator. The computation of TAS spectra involves performing two simulations for recording the dipole moment at each time step; these simulations and their quantities are denoted by \( p \) and \( pp \) subscripts, indicating that the real-time propagation used pump-only pulse and pump together with the probe pulse, respectively. This difference is calculated to isolate the effect of the probe pulse on the non-stationary electronic wavepacket, i.e. to eliminate pump-only-dependent terms in Eq. (7). This procedure is in contrast with the simulations initiated from an equilibrium stationary state (i.e. without pump), for which Eq. (7) simplifies to the static dipole moment that is subtracted in Eq. (22), and the absorption spectra thus only require one time propagation simulation. The differential dipole moment is subsequently transformed into the frequency domain (like in Eq. (6)). Finally, the TAS spectral function \( S_{\text{TAS}}^{\text{ST}}(\omega) \) is evaluated.
analogously to its ground state absorption counterpart as,

\[ S^{\text{TAS}}(\omega) = \frac{4\pi \omega}{3c} \Im \text{Tr}[\alpha^{\text{TAS}}(\omega)] \]

where \( \alpha^{\text{TAS}}_{\text{uv}} = \frac{\Delta \mu^{\text{TAS}}_{\text{uv}}(\omega)}{\mathcal{F}_0} \).

In Eq. (23), \( c \) is the speed of light, \( \text{Tr} \) is a trace over Cartesian components of the polarizability tensor \( \alpha \).

In simulated X-ray spectra, signals originating from transitions between valence and high-lying virtual orbitals can appear. These are non-physical in calculations using finite atom-centered basis sets, since above-ionization states are ill-described in such cases. To eliminate these spurious peaks, we restrict the probe operator to act only on a selected subset of core and virtual orbitals by zeroing all other elements of the dipole matrix when applying the probe pulse thus making the non-physical transitions artificially dipole-forbidden. This technique, called selective perturbation, was introduced in our previous works in the context of XAS calculations using both RT-TDDFT\(^{47}\) as well as damped linear response TDDFT.\(^{61}\)

Note that no restriction is applied on the pump pulse as that is purposefully tuned to an excitation from valence to low-lying orbitals.

In line with the spectral analysis technique for RT–TDDFT simulations presented in Ref. \(^{46}\) we assign the nature of electronic excitations underlying a particular TAS resonance feature by a dipole–weighted transition matrix analysis (DWTA). For a resonant frequency \( \omega' \), the Fourier component \( \mathcal{T}(\omega') \) of the time–domain signal \( \mathcal{T}(t) \) contains all information.

\[ \mathcal{T}(\omega') = \int_0^\infty \mathcal{T}(t + T + \tau)e^{i(\omega' - \Gamma)t}dt ; \quad \mathcal{T}_{\text{uv};ai}(t) = \Delta \mu^{\text{TAS}}_{\text{uv};ai}(t) = \mu^{\text{ind,pp}}_{\text{uv};ai}(t) - \mu^{\text{ind,p}}_{\text{uv};ai}(t). \]

Here, \( a, i \) runs over occupied and virtual spinors, respectively, and we accounted for the fact that only the time signal after the probe pulse is used for the Fourier transform. We use the differential induced dipole moment (Eq (22)) at a specific resonance frequency \( \omega' \), to obtain the contribution of individual occupied–virtual pairs towards the spectral peak. \( \mathcal{T}(t) \) matrix is obtained by averaging over the Cartesian components.
The above formulated RT-TDDFT methodology was implemented in the ReSpect program\textsuperscript{62} and used to investigate the TAS spectra of two prototypical molecules, ethylene and thiophene at the valence and core (L\textsubscript{2,3}) energy region, respectively, employing 1c non-relativistic, 2c amfX2C and 4c Dirac–Coulomb Hamiltonian. Geometries of the systems are given in SI. Uncontracted aug-cc-pVXZ basis set (X=T(C), D(H) for ethylene and T(S), D(C,H) for thiophene)\textsuperscript{67–70} with PBE0–40HF hybrid xc functional\textsuperscript{71} including 40\% exact exchange contributions is used.\textsuperscript{61} For core absorption processes, we use the selective perturbation scheme described above, whereby only electric dipole moment contributions originating from the core S 2p\textsubscript{1/2} and 2p\textsubscript{3/2} orbitals are considered to be dipole-allowed.\textsuperscript{47} The details of the TAS computational setup are elucidated in Table 1 and Figure S1. Note that the choice of direction of polarization of pump pulse (\(n\)) is important as the spectra are sensitive to geometrical features.

Table 1: Computational setup: The pump and probe pulse parameters corresponds to Eq. (1) and (2). Carrier frequency (\(\omega_0\)) is tuned to the first bright excited state along the direction of dipole-allowed transition (\(n\)). Time duration (\(T\)) of the pump pulse corresponds to 15 carrier periods. The pump pulse amplitude (\(E_0\)) is chosen to sufficiently depopulate the ground state. A weak \(\delta\) probe of amplitude \(F_0\) along all the Cartesian components are applied. The probed system is evolved for \(n_{\text{step}}\) with \(\Delta t_{\text{step}}\) length. These parameters are used unless otherwise stated.

| Molecule | \(\omega_0\) (au) | \(T\) (au) | \(n\) | \(E_0\) (au) | \(F_0\) (au) | \(n_{\text{step}}\) | \(\Delta t_{\text{step}}\) (au) |
|----------|------------------|-------------|-------|-------------|-------------|----------------|-------------------|
| C\(_2\)H\(_4\) | 0.2762 | 341.10 | x | 0.01 | 0.01 | 20000 | 0.15 |
| C\(_4\)H\(_4\)S | 0.2135 | 441.20 | y | 0.05 | 0.01 | 25000 | 0.20 |

For ethylene, we study the effect of the degrees of freedom specific to pump-probe processes, focusing on pump pulse strength and pump-probe time delay. Firstly, the effect of pump pulse strength on the TAS spectra is shown in Figure 1. The electronic wavepacket \(|\Psi[\mathcal{E}]\rangle\) generated by the pump pulse comprises of an admixture of ground and excited electronic states (see Eq. (5)), with the effective depopulation of ground state being proportional to \(E_0\). The ground state occupancy at time \(t\) is estimated as \(\text{Tr}[D(0)D(t)]\).\textsuperscript{53} It is evident from Figure 1 that considerable depopulation of ground state is necessary to differentiate
Figure 1: Ethylene – (a) Comparison of UV-vis and TAS spectra with varying $E_0$, given in parentheses, obtained with amfX2C Hamiltonian. TAS is computed at $\tau = 0.0$ with a damping parameter $\Gamma = 0.01\text{ au}$. (b) Variation in the ground state population as a function of simulation time $t$ obtained as $\text{Tr}[D(0)D(t)]$, with pump amplitudes as color coded in (a). $T$ (in red) marks the duration of pump pulse.

TAS spectra from ground state absorption spectra. For exact theory, the ground state population depends only on $\tau$ and $E_0$, and is constant with respect to the simulation time $t$ when the external field is switched-off. However, this does not hold for approximate mean-field methods such as the HF or DFT, where the population oscillates with $t$, as seen in Figure 1b. These artefact oscillations arise as a consequence of the implicit time dependence incorporated in the Fock operator and are attributed to the relaxation of orbitals.\textsuperscript{72–74} TAS spectra of ethylene obtained with $E_0 = 0.01\text{ au}$ is in a good agreement with the pioneering work by Giovannini et al.\textsuperscript{34} using Octopus code.\textsuperscript{75–77} However, due to different computational setup and lack of experimental references we do not focus on a detailed assignment of the TAS spectral features.

From an experimental point-of-view, the most important degree of freedom in TAS is the
Figure 2: Ethylene – (a) Variation in intensity with $\tau$ for the TAS spectral peak at $\omega_0 = 0.2534$ au; (b) Ground state absorption and TAS spectra at $\tau = 0.0$; (c) TAS spectra with varying $\tau$; (d) DWTA of the TAS peak A at $\omega_0 = 0.2534$ au and $\tau = 0.0$. The intensity of blue color corresponds to the intensity of the particular excitation; (e) $\Im \chi_{P_u,P_v}^{\text{int}}[E](0.2534, 341.10+\tau)$ is given in Eq. (25), for degenerate $k, j$ spinor-pair selected as $(15,16)\rightarrow(19,20)$ and $(13,14)\rightarrow(46,45)$ with orbital energy difference of 0.3305 au and 0.6039 au, respectively. White dashed lines corresponds to the resonant $\omega$. $2c$ amfX2C Hamiltonian is used for the RT simulation.
pump–probe time delay $\tau$. The influence of $\tau$ on TAS for ethylene is depicted in Figure 2c.

As the pump pulse is tuned to the first bright state in the ground state absorption spectrum ($A'$ in Figure 2b), this ground state peak is split into peaks $A$, $B$ and $C$ in the TAS. DWTA analysis of $A'$, $A$, $B$ and $C$ (shown in Figure 2d, S3 and S4) shares same dominantly contributing transition of $\pi \rightarrow \pi^*$ character involving degenerate spinor pair (15,16) $\rightarrow$ (19,20). Secondary contributions come from transitions involving degenerate spinor pair (13,14) $\rightarrow$ (46,45). Interestingly, peak $D$ has completely different character from any of the features obtained in the ground state absorption spectra, further emphasising on the novelty of this spectroscopic technique to probe states (and therein molecular orbitals) not directly accessible by purely ground or excited-state absorption.

A striking feature of the TAS spectrum in Figure 2 is the oscillation of spectral intensity with $\tau$. As shown in Figure S5, this feature is not associated with the variation of the contributing orbitals underlying a particular frequency peak with time-delay. Therefore, non-equilibrium response theory was applied to understand qualitatively the origin of these modulations. Considering that the system consists of only light elements (C,H), a reasonable approach is to use only the non-relativistic component associated with the real part of the response function in Eq. (9). As shown in Figure 2d, the DWTA of peak $A$ reveals that only two transitions $[(15,16) \rightarrow (19,20)]$ and $[(13,14) \rightarrow (46,45)]$ with orbital energy difference of 0.3305 au and 0.6039 au contribute. Therefore, only these transitions appear in the summation over $k, j$ in Eq. (9). By discretizing the summation over $m$ such that $\omega_{jm}$ is within the frequency range $[0.0,0.6\text{au}]$, and further assuming that the two transitions: (I) are of equal probability, i.e. $|c_j(\mathcal{E})c_k(\mathcal{E})| = 1$; (II) have zero phase-factor difference ($\phi_j - \phi_k = 0$); (III) have the same electric dipole transition moments for all $m$ ($P_{v,km} = 1$), we arrive at a simplified formula for the response function, plotted in Figure 2e,

$$
\Im\chi_{P_u,P_u}^{\text{int}}[\mathcal{E}](0.2534,341.10 + \tau) = \sum_{\omega_{kj} \in [0.3305,0.6039]} \cos(-\omega_{kj}\tau)\left\{L(0.2534 - \omega_{jm}) - L(0.2534 + \omega_{jm})\right\} \\
+ \sin(-\omega_{kj}\tau)\left\{R(0.2534 - \omega_{jm}) + R(0.2534 + \omega_{jm})\right\}.
$$

(25)
Even with such simplifications, we were able to mimic the appearance of the intensity oscillation with $\tau$, unique to TAS. Especially we are capable of capturing the decrease in intensity at the maxima at $\omega = 0.2534$ au, marked by white dashed line in Figure 2b. Providing more information about initial phase difference and dipole contributions, will enable one to more closely reproduce the spectral feature from response theory.

Figure 3: Thiophene – Ground state L$_{2,3}$-edge X-ray absorption spectra obtained with $1c$ non-relativistic (orange), $2c$ amfX2C (blue) and $4c$ Dirac–Coulomb (cyan) Hamiltonian using a damping factor of $\Gamma = 0.005$ au. The simulated spectra is shifted by +1.42 eV, to match the first experimental peak. Experimental results are digitized from Ref. 78. DWTA analysis of the spectral peaks obtained with $1c$ and $2c$ Hamiltonians are shown in Figures S6 and S7, respectively.

Next, we focus on the energy region of the core L$_{2,3}$-edge of sulphur in thiophene. The experimental and simulated ground state XAS at the non-relativistic ($1c$), amfX2C ($2c$), and Dirac–Coulomb ($4c$) Hamiltonian level are presented in Figure 3, clearly demonstrating the importance of including SO coupling effects to reproduce the doublet structure of the spectra ($B_{III}^{'}, C_{III}^{'}$ versus $B_{II}^{'}$, $C_{II}^{'}$). The DWTA analysis of individual peaks (shown in Figure S6 and S7) reveals that the lower energy feature corresponds to promotion from the S 2$p_{3/2}$, whereas the higher energy ones are from S 2$p_{1/2}$. Each of the SO split band, is further split due to the molecular field (MF), corresponding to $9e_{1/2}$, $8e_{1/2}$ ($L_3$ component) and $7e_{1/2}$ ($L_2$ component) molecular orbitals and leading to the lower energy separated doublets. The MF doublet ($B'$ and $C'$) also appears at the $1c$ level. The SO split counterpart $A_{II}^{'}$ of
Figure 4: Thiophene – (a) TAS at $\tau = 0$ with 1c non-relativistic (orange), 2c amfX2C (blue) and 4c Dirac–Coulomb (cyan) Hamiltonian; (b) Variation in TAS spectra with $\tau$ obtained with 1c non-relativistic Hamiltonian; (c) Variation in TAS spectra with $\tau$ obtained with 2c amfX2C Hamiltonian. All spectra are obtained with a damping factor $\Gamma = 0.01$ au.

band A$^{\prime}$\textsubscript{III} is hidden under the more intense B$^{\prime}$\textsubscript{III} and C$^{\prime}$\textsubscript{III} doublet. The experimental SO splitting of 1.2 eV is well reproduced by our relativistic Hamiltonian. We would like to draw the attention of the readers to the remarkable agreement between the XAS obtained with our amfX2C and gold-standard Dirac–Coulomb Hamiltonian, the former being generated at a fraction of the computational cost of the later. Finally, we compute the TAS spectra using a setup described in Table I and shown in Figure 4. The importance of incorporating relativistic effects is further reinforced here as evident from the SO split doublet spectral peaks generated using the relativistic (2c and 4c) Hamiltonian. Again, the resemblance of the TAS simulated at the 2c and 4c level at $\tau = 0.0$ (see Figure 4a) further gives us confidence to use the modern amfX2C Hamiltonian for larger systems in future studies.

In summary, we have formulated and implemented a theoretical approach for first-
principle simulation of TAS spectra based on relativistic RT-TDDFT frameworks, consistently applicable across the Periodic Table and element-specific core energy regions. Alongside gold-standard four-component methodology, remarkable accuracy and significant computational acceleration was achieved by introducing amfX2C Hamiltonian within RT-TDDFT framework. With this, we identify and interpret the unique features associated with TAS spectra, notably the appearance of negative intensity peaks and oscillations in intensity of a particular energy feature with pump-probe time delay. These observations were further supported by non-equilibrium response theory, relativistic generalization of which was also formulated in this letter. Finally, we showcase fingerprints of spin-orbit effects on the X(T)AS spectra near the sulphur L$_{2,3}$-edge of thiophene. We believe, this work constitutes a significant methodological advancement for studying and interpreting transient absorption spectra, applicable to X-ray regimes and/or heavy systems.

**Acknowledgement**

We acknowledge the support received from the Research Council of Norway through a Centre of Excellence Grant (No. 262695), a Research Grant (No. 315822), and Mobility Grants (No. 301864 and No. 314814), as well as the use of computational resources provided by UNINETT Sigma2 – The National Infrastructure for High Performance Computing and Data Storage in Norway (Grant No. NN4654K). In addition, this project received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement No. 945478 (SASPRO2), and the Slovak Research and Development Agency (Grant No. APVV-21-0497).

**Supporting Information Available**

Real-time propagator; Computational setup; Dependence of TAS on pump pulse carrier frequency; DWTA; Molecular geometries. This information is available free of charge via the
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Figure 5: For Table of Contents Only

\[ \Delta \mu^{\mu \nu}_{\text{TAS}}(t) \equiv \mu^{\mu \nu}_{\text{pp}}(t) - \mu^{\mu \nu}_{\text{p}}(t) \]

- Orange: 1c
- Dashed Blue: 2c
- Cyan: 4c

Intensity (au)

162 163 164 165 166 167 168 169

Energy (eV)

TAS(\tau = 0)