Acceleration of relativistic electron dynamics by means of X2C transformation: application to the calculation of non-linear optical properties

Lukas Konecny,[†] Marius Kadek,[‡] Stanislav Komorovsky,[‡] Olga L. Malkina,[¶,†]
Kenneth Ruud,[‡] and Michal Repisky[*,‡]

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovak Republic, The Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT The Arctic University of Norway, Tromsø, Norway, and Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic

E-mail: michal.repisky@uit.no

Abstract

The Liouville–von Neumann equation based on the four-component matrix Dirac–Kohn–Sham Hamiltonian is transformed to a quasirelativistic exact two-component (X2C) form, and then used to solve the time evolution of the electronic states only. By this means, a significant acceleration by a factor of seven or more has been achieved. The transformation of the original four-component equation of motion is formulated entirely in matrix algebra, following closely the X2C decoupling procedure of Ilias and Saue [J. Chem. Phys. **126**, 064102 (2007)]

---

[*] To whom correspondence should be addressed

[†] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovak Republic

[‡] The Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT The Arctic University of Norway, Tromsø, Norway

[¶] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic

proposed earlier for a static (time-independent) case. In a dynamic (time-dependent) regime, however, an *adiabatic approximation* must in addition be introduced in order to preserve the block-diagonal form of the time-dependent Dirac–Fock operator during the time evolution. The resulting X2C Liouville–von Neumann electron dynamics (X2C-LvNED) is easy to implement as it does not require an explicit form of the picture-change transformed operators responsible for the (higher-order) relativistic corrections and/or interactions with external fields. To illustrate the accuracy and performance of the method, numerical results and computational timings for non-linear optical properties are presented. All the time-domain X2C-LvNED results show excellent agreement with the reference four-component calculations as well as with the results obtained from frequency-domain response theory.

1 Introduction

In non-linear optical (NLO) processes, an external electric field applied to a material induces non-linear responses that are characterized by the (frequency-dependent) hyperpolarizabilities.[1] The wide area of applications of NLO materials have created a demand for accurate theoretical predictions of those properties in order to contribute to the design and optimization of materials with large NLO responses.[2] For molecule-based materials, the majority of the compounds studied to date are organic molecules,[3] including in recent years also organic diradicals.[4,5] However, metal-containing compounds, such as organometallic, coordination or open-shell dimetal compounds, have risen to prominence due to their favourable electric properties, which can be tuned by the metal centers that can serve either as donors or acceptors.[6–8] This has resulted in an increased interest in theoretical methods capable of treating open-shell systems, and in the case of heavy atom-containing molecules also in including relativistic effects, as these are known to be important for reaching high accuracy.

Static (hyper)polarizabilities can be calculated using either finite field methods or analytic derivative techniques, the latter being the preferred option nowadays.[9–11] To calculate dynamical (or frequency-dependent) (hyper)polarizabilities, one can use the sum-over-state (SOS) expression which requires access to the excited states of a system.[12,13] However, the SOS approach often converges slowly with respect to the number of excited states included in the calculation, making such calculations in general difficult. Another option is to solve the time-dependent Schrödinger (or Dirac) equation in the presence of a dynamic external electric field perturbatively, facilitating the linear, quadratic or even higher-order response theory.[14–19] This theory is well suited also for mean-field approaches such as HF and DFT, but may suffer from divergences at (near) resonant frequencies which can be remedied by introducing the complex polarization propagator (CPP) technique.[20,21] An alternate route is to solve the time-dependent Schrödinger (or Dirac) equation directly in the time domain by propagating the electronic density/states in dynamics simulations. This approach has gained popularity in recent years and several studies of NLO properties have been reported at the non-relativistic level of theory.[22–26]

Although real-time electron dynamics is generally considered to be computationally more expensive for molecular property calculations than response theory in the frequency-domain, it is conceptually and implementationally simpler than the latter approach, yields the full spectral window with only a few simulations, does not suffer from divergences at resonant frequencies, and due to its real-time nature might offer additional insight into the excitation processes that occur in molecules subjected to external electromagnetic fields.[27] Although the divergence problems associated with (near)-resonant frequencies can be resolved through the use of the CPP approach, the application of intense radiation, spanning wavelengths from the far-infrared to far-ultraviolet region, may lead to a break-down of the perturbation treatment used in response theory and CPP.

In recent years, several implementations of real-time electron dynamics have been reported in the literature, most of them based on non-relativistic Hamiltonians utilizing either a real-space grid methodology developed by Theilhaber,[28] and pioneered by Yabana and Bertsch,[29] or analytic atom-centered basis functions. Although the calculation of molecular properties by means of real-time dynamics represents a young and conceptually different strategy than response theory, it offers access to a wide range of spectroscopic properties, varying from linear[30–34] and non-linear optical response properties,[22–26] singlet–triplet transitions,[34–36] molecular conductance,[37] electronic[38] and magnetic circular dichroism,[39] X-ray[40–43] and excited-state absorption,[44] to plasmon resonances.[45]

In theoretical simulations involving elements from the lower part of the periodic table, however, inclusion of relativistic corrections is mandatory to reach spectroscopic accuracy. In relativistic quantum chemistry, this is typically achieved by combining the one-electron Dirac operator[46,47] with the instantaneous (non-relativistic) Coulomb interaction, considered as the first approximation to relativistically corrected two-electron interactions.[48,49] Although the four-component treatment represents a natural starting point for coupling the quantum system to the external electromagnetic field, there has been a substantial effort to reduce the methodological as well as the computational complexity by developing two-component (quasirelativistic) Hamiltonians. Among the variationally stable and popular two-component Hamiltonians are the second-order Douglas–Kroll–Hess (DKH2) Hamiltonian,[50–52] the zeroth-order regular approximation (ZORA) Hamiltonian,[53,54] the normalized elimination of small component (NESC) Hamiltonian,[55,56] or the exact two-component (X2C) Hamiltonian.[57–61] In general, the main computational gain of these quasirelativistic methods comes from discarding the negative-energy states, which results in a reduction of the original four-component problem by half and more importantly in abandoning the need to evaluate expensive two-electron integrals over the small-component balanced basis associated with these states. Among the quasirelativistic Hamiltonians, NESC[55,56] and X2C[58–61] have gained popularity in recent years because they allow to reduce the four-component problem to its quasirelativistic form only at the expense of applying simple algebraic manipulations, without the need to generate explicit operator expressions for higher-order relativistic corrections and/or property operators. While the connection between NESC and one-step iterative X2C is recognized,[62] the simplified one-step non-iterative X2C formulation of Ilias and Saue[61] will be adopted here for the formulation of electron dynamics.

In general, the real-time electron dynamics requires considerable computational effort due to the repeated construction of the Fock matrix at each time interval, and this computational burden increases even more for implementations based on the four-component methodology, in particular if the problem of interest involves long simulation times and/or many time steps. The fully relativistic implementation of the dynamics has recently been pursued in our group and applied to the calculation of absorption spectra, both in the valence[34] and X-ray regions.[42] In the present work, we extend the existing relativistic methodology by coupling real-time electron dynamics based on the Liouville–von Neumann equation with the X2C Hamiltonian. This leads to a significant acceleration of the relativistic real-time dynamics while still including both the scalar and spin-orbit relativistic corrections variationally. As we shall demonstrate for NLO properties, the data obtained by this method are in excellent agreement with reference four-component results.

The article is organized as follows: In Section 2.1, we introduce the X2C decoupling transformation of the four-component equation of motion to its quasirelativistic two-component form and review the basic methodology used to solve this equation in our program. In Section 2.2, we summarize a procedure for extracting NLO properties from induced dipole moments introduced earlier by Ding *et al.*,[26] followed by all the implementation details in Section 3. Computational aspects are given in Section 4 and both the accuracy and performance of the method are illustrated by calculations of NLO properties in Section 5. Finally, concluding remarks and perspectives are drawn in Section 6.

2 Theory

2.1 X2C transformation of the time-dependent Dirac equation

In the following, we will discuss details of the time-dependent relativistic theory based on the X2C Hamiltonian. For the sake of transparency, we start this discussion by considering the equation of motion (EOM) for the molecular orbital (MO) coefficients (in atomic units)

$$i\frac{\partial}{\partial t}\mathbf{C}(t) = \mathbf{F}(t)\mathbf{C}(t). \tag{1}$$

In the formalism of Hartree–Fock or Kohn–Sham DFT theory, $\mathbf{F}(t)$ is the matrix representation of the time-dependent Fock operator in an orthonormal basis whereas $\mathbf{C}(t)$ is the matrix of time-dependent MO coefficients. In relativistic four-component theory, the matrices $\mathbf{F}(t) = \mathbf{F}^{4\mathrm{C}}(t)$ and $\mathbf{C}(t) = \mathbf{C}^{4\mathrm{C}}(t)$ are represented over the field of complex numbers $\mathbb{C}$ and have the dimension $4n \times 4n$, where n denotes the number of scalar basis functions. In order to accelerate the solution of Eq. (1) we can, in the spirit of the time-independent X2C formalism,[59–61] seek for a unitary matrix $\mathbf{U}(t)$ that block-diagonalizes (decouples) the parent Fock matrix at any given time

$$\mathbf{F}^{4\mathrm{C}}(t) := \begin{pmatrix} \mathbf{F}^{\mathrm{LL}} & \mathbf{F}^{\mathrm{LS}} \\ \mathbf{F}^{\mathrm{SL}} & \mathbf{F}^{\mathrm{SS}} \end{pmatrix} \quad \longrightarrow \quad \mathbf{F}^{\mathrm{X2C}}(t) := \mathbf{U}^{\dagger}(t)\mathbf{F}^{4\mathrm{C}}(t)\mathbf{U}(t) = \begin{pmatrix} \mathbf{F}_{+}^{\mathrm{X2C}} & 0 \\ 0 & \mathbf{F}_{-}^{\mathrm{X2C}} \end{pmatrix}. \tag{2}$$

The unitary matrix $\mathbf{U}(t)$ transforms Eq. (1) to

$$i\frac{\partial}{\partial t}\mathbf{C}^{\mathrm{X2C}}(t) = \mathbf{F}^{\mathrm{X2C}}(t)\mathbf{C}^{\mathrm{X2C}}(t) + i\left(\frac{\partial}{\partial t}\mathbf{U}^{\dagger}(t)\right)\mathbf{U}(t)\mathbf{C}^{\mathrm{X2C}}(t), \tag{3}$$

where $\mathbf{C}^{\mathrm{X2C}}(t) := \mathbf{U}^{\dagger}(t)\mathbf{C}^{4\mathrm{C}}(t)$. Let us assume we know the initial condition for Eq. (3) at time t_0, which in the X2C formalism results in a block-diagonal form for $\mathbf{C}^{\mathrm{X2C}}(t_0)$:

$$\mathbf{C}^{\mathrm{X2C}}(t_0) := \mathbf{U}^{\dagger}(t_0)\mathbf{C}^{4\mathrm{C}}(t_0) = \begin{pmatrix} \mathbf{C}_{+}^{\mathrm{X2C}} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}_{-}^{\mathrm{X2C}} \end{pmatrix}. \tag{4}$$

Here, the superscripts L and S refer to the large and small component of the four-component orthonormal basis functions, whereas the subscripts $+$ and $-$ refer to the positive- and negative-energy domains of the Dirac–Fock eigenvalue spectrum. Note, however, that the X2C transformed EOM, Eq. (3), is not fully decoupled due to the term containing the time derivative of the unitary transformation matrix, $\partial\mathbf{U}^{\dagger}/\partial t$, and thus, the MO coefficients do not retain their block diagonal structure during the time evolution. Next follows the discussion how we achieve the X2C decoupling transformation of Eq. (3).

The time evolution of the transformed MO coefficients ($\mathbf{C}^{\mathrm{X2C}}$) obtained from Eq. (3) is equivalent to the propagation of $\mathbf{C}^{4\mathrm{C}}$ using Eq. (1), provided $\mathbf{U}(t)$ and $\partial\mathbf{U}^{\dagger}/\partial t$ are known at each time. If the Fock matrix $\mathbf{F}^{\mathrm{X2C}}$ is expressed as a sum of X2C transformed one-electron ($\mathbf{h}^{\mathrm{X2C}}$), two-electron ($\mathbf{g}^{\mathrm{X2C}}$), and time-dependent external field contributions ($\mathbf{V}^{\mathrm{ext,\,X2C}}$), then the X2C unitary decoupling matrix $\mathbf{U}$ block-diagonalizes only the one-electron term. By this, the dominant part of the scalar and spin-orbit corrections originating from the electron–nuclear attraction potential are included. In general, it is also possible to add into the construction of $\mathbf{U}$ additional relativistic corrections arising from two-electron interactions, but in order to get the full computational benefit of the two-component formalism, this can be done only approximately from atomic calculations.[63–66] The exclusion of two-electron contributions from a picture-change transformation is a common approximation used in two-component methods, and this is denoted as a *bare nucleus* X2C approximation (nucX2C) in our program. In the present work, we explore this route and approximate the two-electron contribution ($\mathbf{g}$) by untransformed four-component LL-block: $\mathbf{g}^{\mathrm{X2C}} = \mathbf{U}^{\dagger}\mathbf{g}^{4\mathrm{C}}\mathbf{U} \approx \mathbf{g}^{4\mathrm{C,LL}} := \mathbf{g}^{\mathrm{LL}}$ (for more discussion, see also Refs.[64,65]). The remaining terms in Eq. (3), $\mathbf{V}^{\mathrm{ext,\,X2C}}$ and $\dot{\mathbf{U}}^{\dagger}\mathbf{U}$ (where $\dot{\mathbf{U}} \equiv \partial\mathbf{U}/\partial t$), have non-zero off-diagonal blocks that prevents a complete decoupling of the X2C transformed EOM. In the presence of an external oscillating field of frequency ω, however, the amplitude of the latter term can be estimated as

$$\dot{\mathbf{U}}^{\dagger}\mathbf{U} \approx -\begin{pmatrix} \mathbf{0} & -\dot{\mathbf{R}}^{\dagger} \\ \dot{\mathbf{R}} & \mathbf{0} \end{pmatrix} = \mathscr{O}(\omega c^{-1}). \tag{5}$$

The matrix $\mathbf{R}$ parametrizes the decoupling matrix $\mathbf{U}$, as defined by time-dependent variant of Eqs. (6), and for positive energy states it is of order $\mathscr{O}(c^{-1})$. The term in Eq. (5) can be safely neglected within the dipole approximation, where $\omega\, l\, c^{-1} \ll 1$, with l representing the molecular size of several Bohrs. Beyond the dipole approximation, $\omega\, c^{-1} \ll 1$ can still be valid for low-frequency fields, however, care must be taken for fields with high frequency. The neglect of updating $\mathbf{U}$ during the time propagation, denoted in the following text as *adiabatic approximation*, *i.e.* $\mathbf{U}(t) \approx \mathbf{U}(t_0)$, is analogous to performing the X2C decoupling transformation in the time-independent self-consistent field (SCF) procedure only once at the initial stage of the SCF iterations. For the matrix of the time-dependent external field operator ($\mathbf{V}^{\text{ext, X2C}}$), we perform a picture-change transformation and discard the off-diagonal blocks: $\mathbf{V}^{\text{ext,X2C}} = \mathbf{U}^{\dagger}(\mathbf{V}^{\text{ext,4C}})\mathbf{U} \approx \text{diag}\left(\mathbf{V}_{+}^{\text{ext,X2C}}, \mathbf{V}_{-}^{\text{ext,X2C}}\right)$. The latter approximation can be justified by the fact that the potential describing the electric field $\mathbf{V}^{\text{ext,X2C}}$, as a source of perturbation, has off-diagonal terms of order c^{-1} and causes at any given time a change in the electric dipole moments only of the order c^{-2}. By means of all these approximations, we have achieved a decoupling of the EOM in Eq. (3). To conclude, the proposed procedure leads to a decoupling of the original four-component EOM and it requires a sequence of approximations in order to make the quasirelativistic method efficient, easy to implement and of practical use. Similar approximations are also common in the static (time-independent) theory.

Based on the arguments in the previous paragraph, the decoupling operator $\mathbf{U}$ is considered time-independent and can be constructed using methods developed in the context of time-independent X2C approaches. As proposed by Kutzelnigg,[67] $\mathbf{U}$ can be divided into a decoupling matrix $\mathbf{W}_1$ and a renormalization matrix $\mathbf{W}_2$, both of which are parametrized by a single matrix $\mathbf{R} \in \mathbb{C}_{2n\times 2n}$ as shown by Heully *et al.*,[57]

$$\mathbf{U} := \mathbf{W}_1\mathbf{W}_2 \tag{6a}$$

$$\mathbf{W}_1 := \begin{pmatrix} \mathbf{I} & -\mathbf{R}^{\dagger} \\ \mathbf{R} & \mathbf{I} \end{pmatrix}; \quad \mathbf{W}_2 := \begin{pmatrix} \mathbf{W}_2^{+} & \mathbf{0} \\ \mathbf{0} & \mathbf{W}_2^{-} \end{pmatrix} = \begin{pmatrix} (\mathbf{I}+\mathbf{R}^{\dagger}\mathbf{R})^{-1/2} & \mathbf{0} \\ \mathbf{0} & (\mathbf{I}+\mathbf{R}\mathbf{R}^{\dagger})^{-1/2} \end{pmatrix}. \tag{6b}$$

The transformed coefficients $\mathbf{C}^{\text{X2C}}$ in Eq. (4) have the general form

$$\mathbf{C}^{\text{X2C}} = \mathbf{W}_2^{\dagger} \begin{pmatrix} \mathbf{C}_{+}^{\text{L}} + \mathbf{R}^{\dagger}\mathbf{C}_{+}^{\text{S}} & \mathbf{C}_{-}^{\text{L}} + \mathbf{R}^{\dagger}\mathbf{C}_{-}^{\text{S}} \\ \mathbf{C}_{+}^{\text{S}} - \mathbf{R}\mathbf{C}_{+}^{\text{L}} & \mathbf{C}_{-}^{\text{S}} - \mathbf{R}\mathbf{C}_{-}^{\text{L}} \end{pmatrix}. \tag{7}$$

and, in order for the $\mathbf{C}^{\mathrm{X2C}}$ matrix to be block-diagonal, the matrix $\mathbf{R}$ must satisfy the conditions

$$\mathbf{C}_{+}^{\mathrm{S}} - \mathbf{R}\mathbf{C}_{+}^{\mathrm{L}} = 0, \tag{8a}$$

$$\mathbf{C}_{-}^{\mathrm{L}} + \mathbf{R}^{\dagger}\mathbf{C}_{-}^{\mathrm{S}} = 0. \tag{8b}$$

The solution of the linear algebraic equations Eq. (8), as shown by Ilias and Saue, represents a simple non-iterative one-step approach to determine $\mathbf{R}$.[61] An alternative procedure that facilitates the solution of a quadratic equation derived from the time-independent form of Eq. (2) has been proposed by Kutzelnigg and Liu.[59,60] However, due to its conceptual simplicity, we will follow the approach of Ilias and Saue in the present work. The matrix $\mathbf{U}$ in Eq. (6) can be interpreted as a transformation matrix from an original orthonormal four-component RKB basis to a new orthonormal four-component X2C basis in which the off-diagonal blocks of the Fock matrix are zero.

Finally, after discarding the negative-energy solutions, the X2C equation of motion (X2C-EOM) for the positive-energy solutions reads

$$\begin{aligned} i\frac{\partial}{\partial t}\,\mathbf{C}_{+}^{\mathrm{X2C}}(t) &= \mathbf{F}_{+}^{\mathrm{X2C}}(t)\;\mathbf{C}_{+}^{\mathrm{X2C}}(t) \\ &= (\mathbf{W}_{2}^{+})^{\dagger}\left[\mathbf{F}^{\mathrm{LL}}(t) + \mathbf{F}^{\mathrm{LS}}(t)\mathbf{R} + \mathbf{R}^{\dagger}\mathbf{F}^{\mathrm{SL}}(t) + \mathbf{R}^{\dagger}\mathbf{F}^{\mathrm{SS}}(t)\mathbf{R}\right]\mathbf{W}_{2}^{+}\;\mathbf{C}_{+}^{\mathrm{X2C}}(t), \end{aligned} \tag{9}$$

with the two-component X2C Fock operator

$$\mathbf{F}_{+}^{\mathrm{X2C}}(t) = \mathbf{h}_{+}^{\mathrm{X2C}} + \mathbf{g}^{\mathrm{LL}}(t) + \mathbf{V}_{+}^{\mathrm{ext,X2C}}(t). \tag{10}$$

Note that the dimension of the introduced X2C-EOM is only half of the original four-component EOM and can be written in an equivalent manner in the density-matrix formalism as the X2C transformed Liouville–von Neumann equation:

$$i\frac{\partial}{\partial t}\mathbf{D}_{+}^{\mathrm{X2C}}(t) = [\mathbf{F}_{+}^{\mathrm{X2C}}(t), \mathbf{D}_{+}^{\mathrm{X2C}}(t)]. \tag{11}$$

We have here introduced the X2C time-dependent one-electron reduced density matrix

$$\mathbf{D}_{+}^{\mathrm{X2C}}(t) = \mathbf{C}_{+}^{\mathrm{X2C}}(t)\left(\mathbf{C}_{+}^{\mathrm{X2C}}(t)\right)^{\dagger}, \tag{12}$$

where we implicitly assumed that the summation only runs over the occupied set of MOs. The density matrix in Eq. (12) has form equivalent to its time-independent counterpart, reflecting the fact that the time-evolved wave function has the form of a single Slater determinant at all times.

Our implementation of X2C-EOM in the program `ReSpect` facilitates the Liouville–von Neumann equation in the density matrix formalism Eq. (11), whose general solution can be expressed via the evolution operator $\boldsymbol{\mathcal{U}}$:

$$\mathbf{D}_{+}^{\mathrm{X2C}}(t) = \boldsymbol{\mathcal{U}}(t,t_0)\,\mathbf{D}_{+}^{\mathrm{X2C}}(t_0)\,\boldsymbol{\mathcal{U}}^{\dagger}(t,t_0); \qquad \boldsymbol{\mathcal{U}}(t,t_0) = \mathscr{T}\exp\left[-i\int_{t_0}^{t}\mathbf{F}_{+}^{\mathrm{X2C}}(\tau)d\tau\right]. \tag{13}$$

The evolution operator contains the time-ordered exponential ($\mathscr{T}$ exp), which is difficult to evaluate numerically. Various propagator techniques have therefore been developed, in most cases relying on the division of the time interval into short time steps and reformulation and truncation of the expression for $\boldsymbol{\mathcal{U}}$.[68,69] We use the second-order midpoint Magnus method,[70] which is based on replacing the time ordering in the expression for the evolution operator in Eq. (13) by an infinite series, and then truncating the series after its first term, which gives rise to an evolution operator of the form

$$\boldsymbol{\mathcal{U}}(t+\Delta t,t) \approx \exp\left[-i\mathbf{F}_{+}^{\mathrm{X2C}}\left(t+\frac{\Delta t}{2}\right)\cdot\Delta t\right]. \tag{14}$$

The operator in Eq. (14) describes the time evolution of the density matrix over a short time step Δt, and the overall time evolution is carried throughout a series of small time propagations. The Fock matrix $\mathbf{F}_{+}^{\mathrm{X2C}}(t+\Delta t/2)$ used to construct the evolution operator in Eq. (14) depends on a yet unknown density matrix associated with the future time, $t+\Delta t/2$. In order to solve this apparent self-consistent problem, and to ensure numerical stability and robustness of the time propagation, we employ an iterative extrapolation-interpolation scheme[33,34] (see Section 3 for more details).

The same time propagation procedure has been used earlier at the one- and four-component levels of theory for simulating absorption spectra in both valence[34] and X-ray regions.[42]

2.2 The calculation of molecular (hyper)polarizabilities

When a molecule is subjected to a time-dependent external electric field $\mathbf{E}(t)$, an electric dipole moment $\boldsymbol{\mu}(t)$ is induced and its Taylor expansion in powers of the external field reads

$$\begin{aligned}\mu_i(t) = &\int_{-\infty}^{t} dt_1 \alpha_{ij}(t-t_1)E_j(t_1) \\ &+ \frac{1}{2!}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \beta_{ijk}(t-t_1,t-t_2)E_j(t_1)E_k(t_2) \\ &+ \frac{1}{3!}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_3 \gamma_{ijkl}(t-t_1,t-t_2,t-t_3)E_j(t_1)E_k(t_2)E_l(t_3) + \dots \end{aligned} \tag{15}$$

where $\alpha_{ij}(t)$, $\beta_{ijk}(t_1,t_2)$, $\gamma_{ijkl}(t_1,t_2,t_3)$ are the time-dependent polarizability, first hyperpolarizability and second hyperpolarizability tensors. Here, Einstein's summation convention is assumed. To extract individual frequency-dependent NLO properties from the time-dependent tensors, we follow the procedure by Ding *et al.*,[26] and divide the external field into a time-dependent scalar function and a time-independent vector amplitude, $E_j(t) = F(t)A_j$. This allows us to rewrite Eq. (15) as a Taylor series in powers of the external field amplitudes

$$\mu_i(t) = \mu_{ij}^{(1)}(t)A_j + \mu_{ijk}^{(2)}(t)A_jA_k + \mu_{ijkl}^{(3)}(t)A_jA_kA_l + \dots \tag{16}$$

from which the n'th-order susceptibilities $\mu^{(n)}$ can be extracted as n'th-order derivatives of the induced dipole moment

$$\mu^{(1)}_{ij}(t) = \left.\frac{\partial \mu_i(t)}{\partial A_j}\right|_{\boldsymbol{A}=0} = \int_{-\infty}^{t} dt_1\ \alpha_{ij}(t-t_1)F(t_1), \tag{17a}$$

$$\mu^{(2)}_{ijk}(t) = \left.\frac{1}{2!}\frac{\partial^2 \mu_i(t)}{\partial A_j \partial A_k}\right|_{\boldsymbol{A}=0} = \frac{1}{2!}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2\ \beta_{ijk}(t-t_1,t-t_2)F(t_1)F(t_2), \tag{17b}$$

$$\mu^{(3)}_{ijkl}(t) = \left.\frac{1}{3!}\frac{\partial^3 \mu_i(t)}{\partial A_j \partial A_k \partial A_l}\right|_{\boldsymbol{A}=0} = \frac{1}{3!}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_3\ \gamma_{ijkl}(t-t_1,t-t_2,t-t_3)F(t_1)F(t_2)F(t_3). \tag{17c}$$

By choosing a harmonic (cosine) time dependence of the external field, $F_j(t) = \cos(\omega t)$, we can recognize the Fourier components of the time-dependent (hyper)polarizabilities in the integrals of Eq. (17). The resulting formulas, that express the time-dependent susceptibilities via the frequency-dependent (hyper)polarizabilities, are then

$$\mu^{(1)}_{ij}(t) = \alpha_{ij}(-\omega;\omega)\cos(\omega t), \tag{18a}$$

$$\mu^{(2)}_{ijk}(t) = \frac{1}{4}\left[\beta_{ijk}(-2\omega;\omega,\omega)\cos(2\omega t) + \beta_{ijk}(0;\omega,-\omega)\right], \tag{18b}$$

$$\mu^{(3)}_{ijkl}(t) = \frac{1}{24}\left[\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)\cos(3\omega t) + 3\bar{\gamma}_{ijkl}(-\omega;\omega,\omega,-\omega)\cos(\omega t)\right]. \tag{18c}$$

The frequency-dependent (hyper)polarizabilities are determined by fitting the susceptibilities obtained from different electron dynamics calculations to the expressions on the right-hand side of Eq. (18). These fitting coefficients are related to molecular properties accessible in different NLO experiments; namely, the frequency-dependent polarizability $\alpha_{ij}(-\omega;\omega)$ related to the refractive index, the frequency-dependent first hyperpolarizabilities $\beta_{ijk}(-2\omega;\omega,\omega)$ and $\beta_{ijk}(0;\omega,-\omega)$ related to the second harmonic generation (SHG) and optical rectification (OR) processes, and frequency-dependent second-order hyperpolarizabilities $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ and $\bar{\gamma}_{ijkl}(-\omega;\omega,\omega,-\omega)$ related to third-harmonic generation (THG) and the averaged degenerate four-wave mixing (DFWM) processes. In the present work, the time-dependent susceptibilities in Eq. (17) were determined by a finite-difference scheme, calculating in each time step the central derivatives of induced dipole moments obtained from different electron-dynamics simulations with varying strengths for the external electric fields. The corresponding formulas for the derivatives are summarized in Section 3.

3 Implementation details

In this section we present the algorithm implemented in the TDSCF module of the relativistic DFT program package `ReSpect`,[71] and used to solve the X2C-EOM and to evaluate the NLO properties as described in Section 2.

As the initial step, we solve the X2C time-independent SCF equation to obtain a reference (ground-state) one-electron reduced density matrix. This involves

- evaluating the four-component one-electron Dirac Hamiltonian matrix ($\mathbf{h}^{4\mathrm{C}}$) prior to the SCF iterations. $\mathbf{h}^{4\mathrm{C}}$ is a $\mathbb{C}_{4n\times 4n}$ matrix

  $$\mathbf{h}^{4\mathrm{C}} = \begin{bmatrix} \boldsymbol{h}^{\mathrm{LL}} & \boldsymbol{h}^{\mathrm{LS}} \\ \boldsymbol{h}^{\mathrm{SL}} & \boldsymbol{h}^{\mathrm{SS}} \end{bmatrix} := \begin{bmatrix} \mathbf{V}^{\mathrm{Ne}} & \mathbf{T} \\ \mathbf{T} & \left(\frac{1}{4c^2}\mathbf{W}^{\mathrm{Ne}} - \mathbf{T}\right) \end{bmatrix}, \tag{19}$$

  where $\mathbf{T}$ is the kinetic energy operator matrix, and $\mathbf{V}^{\mathrm{Ne}}$ and $\mathbf{W}^{\mathrm{Ne}}$ denote the matrix representation of the nuclear–electron potential-energy operator over the large-component ($\boldsymbol{X}^{\mathrm{L}} = \{X_1^{\mathrm{L}}, ..., X_n^{\mathrm{L}}\}$) and small-component ($\boldsymbol{X}^{\mathrm{S}} = \{X_1^{\mathrm{S}}, ..., X_n^{\mathrm{S}}\}$) basis. Both $\boldsymbol{X}^{\mathrm{L}}$ and $\boldsymbol{X}^{\mathrm{S}}$ are two-component spinor sets with elements governed to lowest order in c^{-2} by the restricted kinetic balance (RKB) relation[72]

  $$X_\lambda^{\mathrm{L}} := X_\lambda^{\mathrm{L}}(\boldsymbol{r}) = \sigma_0\, \chi_\lambda(\boldsymbol{r}), \qquad X_\lambda^{\mathrm{S}} := X_\lambda^{\mathrm{S,RKB}}(\boldsymbol{r}) = \frac{1}{2c}(\boldsymbol{\sigma}\cdot\boldsymbol{p})\, \chi_\lambda(\boldsymbol{r}), \tag{20}$$

  where σ_0 and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the unit 2×2 matrix and the vector of Pauli spin matrices, respectively. The functions $\chi_\lambda(\mathbf{r})$ are elements of a scalar basis set.

- transforming the one-electron Dirac Hamiltonian Eq. (19) to an orthonormal basis and finding its eigenvectors

$$\begin{bmatrix} \boldsymbol{S} & 0 \\ 0 & \frac{1}{2c^2}\boldsymbol{T} \end{bmatrix}^{-1/2} \begin{bmatrix} \boldsymbol{h}^{\text{LL}} & \boldsymbol{h}^{\text{LS}} \\ \boldsymbol{h}^{\text{SL}} & \boldsymbol{h}^{\text{SS}} \end{bmatrix} \begin{bmatrix} \boldsymbol{S} & 0 \\ 0 & \frac{1}{2c^2}\boldsymbol{T} \end{bmatrix}^{-1/2} \begin{bmatrix} \mathbf{C}_+^{\text{L}} & \mathbf{C}_-^{\text{L}} \\ \mathbf{C}_+^{\text{S}} & \mathbf{C}_-^{\text{S}} \end{bmatrix} = \begin{bmatrix} \mathbf{C}_+^{\text{L}} & \mathbf{C}_-^{\text{L}} \\ \mathbf{C}_+^{\text{S}} & \mathbf{C}_-^{\text{S}} \end{bmatrix} \boldsymbol{\varepsilon}, \tag{21}$$

from which we construct the X2C decoupling matrix, $\mathbf{U}(\mathbf{R})$. Here, we used the Löwdin symmetric orthonormalization, which has a block-diagonal structure in the RKB basis, with the nonrelativistic overlap matrix $\mathbf{S} = \langle \mathbf{X}^{\text{L}} | \mathbf{X}^{\text{L}} \rangle$ and the kinetic energy matrix $\mathbf{T} = \langle \mathbf{X}^{\text{S}} | c(\boldsymbol{\sigma} \cdot \boldsymbol{p}) | \mathbf{X}^{\text{L}} \rangle$ on the diagonal. The choice of a orthonormal basis was made to ensure numerical stability, although the X2C procedure works also for a non-orthonormalized basis.

- from the eigenvectors in Eq. (21), evaluating $\mathbf{R} \in \mathbb{C}_{2n\times 2n}$ by means of a Cholesky decomposition facilitating

$$\mathbf{A}\mathbf{R} = \mathbf{B} \quad \text{where} \quad \mathbf{A} = \mathbf{C}_-^{\text{S}} \mathbf{C}_-^{\text{S}^\dagger}, \quad \mathbf{B} = -\mathbf{C}_-^{\text{S}} \mathbf{C}_-^{\text{L}^\dagger}, \tag{22}$$

derived from Eq. (8b). Note that the matrices $\mathbf{R}$ and $\mathbf{C}$ are represented in an orthonormal basis.

- calculating $\mathbf{U} \in \mathbb{C}_{4n\times 4n}$ from Eq. (6) as the product of the decoupling matrix $\mathbf{W}_1$ and the renormalization matrix $\mathbf{W}_2$. Instead of using Eq. (6b), $\mathbf{W}_2$ is obtained as the solution of

$$\mathbf{W}_2^\dagger \mathbf{M} \mathbf{W}_2 = \mathbf{I}; \qquad \mathbf{M} = \mathbf{W}_1^\dagger \mathbf{W}_1. \tag{23}$$

- after decoupling $\mathbf{h}^{\text{4C}}$ by means of the matrix $\mathbf{U}$, discarding the negative-energy block and solving the two-component time-independent SCF equations

$$\left(\mathbf{h}_+^{\text{X2C}} + \mathbf{g}^{\text{LL}} \right) \mathbf{C}_+^{\text{X2C}} = \mathbf{C}_+^{\text{X2C}} \boldsymbol{\varepsilon}. \tag{24}$$

The two-electron interaction matrix $\mathbf{g}$ was left “picture-change” untransformed as discussed in Section 2.1.

The algorithm outlined for constructing the X2C transformation is similar to the one originally proposed by Ilias and Saue[61] and that described by Peng and co-workers.[73]

The real-time electron dynamics simulations start from the reference time-independent SCF density matrix constructed from the converged $\mathbf{C}_{+}^{\mathrm{X2C}}$ solutions of Eq. (24) using Eq. (12). The molecular system is then perturbed by a picture-change transformed time-dependent external potential $\mathbf{V}_{+}^{\mathrm{ext,X2C}}(t)$ (see Eq. (10)) and propagated according to the X2C Liouville–von Neumann equation (11) in the same spirit as in our earlier fully relativistic four-component studies.[34,42] The density matrix is evolved in time applying the second-order mid-point Magnus propagator (see Eqs. (13) and (14)) with the mid-point Fock matrix calculated from an iterative extrapolation–interpolation scheme.[33,34] This scheme involves the following steps:

- the mid-point Fock matrix is obtained by extrapolating from previous times

$$\mathbf{F}_{+}^{\mathrm{X2C}}\left(t+\frac{\Delta t}{2}\right) = 2\mathbf{F}_{+}^{\mathrm{X2C}}(t) - \mathbf{F}_{+}^{\mathrm{X2C}}\left(t-\frac{\Delta t}{2}\right). \tag{25}$$

- the density matrix $\mathbf{D}_{+}^{\mathrm{X2C}}(t+\Delta t)$ is calculated by applying the evolution operator in Eq. (14) and then used to obtain the corresponding Fock matrix $\mathbf{F}_{+}^{\mathrm{X2C}}(t+\Delta t)$.

- a new mid-point Fock matrix is constructed by interpolation

$$\mathbf{F}_{+}^{\mathrm{X2C}}\left(t+\frac{\Delta t}{2}\right) = \frac{1}{2}\mathbf{F}_{+}^{\mathrm{X2C}}(t) + \frac{1}{2}\mathbf{F}_{+}^{\mathrm{X2C}}(t+\Delta t). \tag{26}$$

The calculation of the $\mathbf{D}_{+}^{\mathrm{X2C}}(t+\Delta t)$ and $\mathbf{F}_{+}^{\mathrm{X2C}}(t+\Delta t)$ matrices and the interpolation step are repeated until convergence is reached. The convergence criterion is the Euclidean norm of the difference between density matrices obtained in the n'th and $(n+1)$'th iteration being lower than some predefined threshold. The converged density matrix $\mathbf{D}_{+}^{\mathrm{X2C}}(t)$ enters in the calculation of the induced dipole moment

$$\boldsymbol{\mu}^{\mathrm{ind}}(t) = \mathrm{Tr}\left[\mathbf{P}_{+}^{\mathrm{X2C}}\,\mathbf{D}_{+}^{\mathrm{X2C}}(t)\right] - \boldsymbol{\mu}^{\mathrm{static}}, \tag{27}$$

where $\mathbf{P}_{+}^{\mathrm{X2C}}$ is the positive-energy block of the X2C transformed electric dipole moment operator matrix. The static dipole moment $\boldsymbol{\mu}^{\mathrm{static}}$ was evaluated at the initial time, t_0.

The NLO properties were extracted from the time evolution of the induced electric dipole moments using numerical derivatives with respect to the amplitudes of the external electric field (see Eq. (17)). For this we carried out several simulations with different external field strengths. For example, the extraction of $\mu_{ij}^{(1)}$ and $\mu_{ijj}^{(2)}$ requires two simulations with amplitudes A_j and $-A_j$ along the Cartesian direction j. Off-diagonal components such as $\mu_{ijk}^{(2)}$ require the simultaneous application of external fields in the Cartesian directions j and k. Unless otherwise stated, the corresponding formulas for the central numerical derivatives with precision of $\mathscr{O}(A^2)$ were used[74]

$$\mu_{ij}^{(1)}(t) = \frac{1}{2A_j}\left[\mu_i^{\mathrm{ind}}(t,A_j) - \mu_i^{\mathrm{ind}}(t,-A_j)\right], \tag{28a}$$

$$\mu_{ijj}^{(2)}(t) = \frac{1}{A_j^2}\left[\mu_i^{\mathrm{ind}}(t,A_j) + \mu_i^{\mathrm{ind}}(t,-A_j)\right], \tag{28b}$$

$$\mu_{ijk}^{(2)}(t) = \frac{1}{2A_k}\left[\mu_{ij}^{(1)}(t,A_k) - \mu_{ij}^{(1)}(t,-A_k)\right], \tag{28c}$$

$$\mu_{ijjj}^{(3)}(t) = \frac{1}{2A_j^3}\left\{2\left[\mu_i^{\mathrm{ind}}(t,-A_j) - \mu_i^{\mathrm{ind}}(t,A_j)\right] - \left[\mu_i^{\mathrm{ind}}(t,-2A_j) - \mu_i^{\mathrm{ind}}(t,2A_j)\right]\right\}. \tag{28d}$$

In order to test the sensitivity of the NLO properties to the precision of the numerical differentiations, we also evaluated the properties with higher $\mathscr{O}(A^4)$ precision, using the formulas[74]

$$\mu_{ij}^{(1)}(t) = \frac{1}{12A_j}\left\{8\left[\mu_i^{\mathrm{ind}}(t,A_j) - \mu_i^{\mathrm{ind}}(t,-A_j)\right] - \left[\mu_i^{\mathrm{ind}}(t,2A_j) - \mu_i^{\mathrm{ind}}(t,-2A_j)\right]\right\}, \tag{29a}$$

$$\mu_{ijj}^{(2)}(t) = \frac{1}{12A_j^2}\left\{16\left[\mu_i^{\mathrm{ind}}(t,A_j) + \mu_i^{\mathrm{ind}}(t,-A_j)\right] - \left[\mu_i^{\mathrm{ind}}(t,2A_j) + \mu_i^{\mathrm{ind}}(t,-2A_j)\right]\right\}, \tag{29b}$$

$$\mu_{ijk}^{(2)}(t) = \frac{1}{12A_k}\left\{8\left[\mu_{ij}^{(1)}(t,A_k) - \mu_{ij}^{(1)}(t,-A_k)\right] - \left[\mu_{ij}^{(1)}(t,2A_k) - \mu_{ij}^{(1)}(t,-2A_k)\right]\right\}, \tag{29c}$$

$$\begin{aligned}\mu_{ijjj}^{(3)}(t) = \frac{1}{8A_j^3}\Big\{&13\left[\mu_i^{\mathrm{ind}}(t,-A_j) - \mu_i^{\mathrm{ind}}(t,A_j)\right] + 8\left[\mu_i^{\mathrm{ind}}(t,2A_j) - \mu_i^{\mathrm{ind}}(t,-2A_j)\right]\\ &+ \left[\mu_i^{\mathrm{ind}}(t,-3A_j) - \mu_i^{\mathrm{ind}}(t,3A_j)\right]\Big\},\end{aligned} \tag{29d}$$

and with the precision $\mathscr{O}(A^6)$ for which the respective formulas are available in the Supporting Information. Finally, all the induced electric dipole moment derivatives were fitted to the analytic formulas Eq. (18) using the non-linear least squares method available in the SciPy library.[75]

4 Computational details

We have evaluated the NLO responses of several molecules using both Liouville–von Neumann electron dynamics (LvNED) and response theory (RT), both at the Hartree–Fock and density functional levels of theory. All the electron dynamics calculations were performed using the relativistic quantum-chemical DFT program `ReSpect`[71] and all the response theory calculations were performed with the `Dalton` program.[76,77] The DFT results were obtained with the non-relativistic adiabatic exchange–correlation (XC) functional of hybrid type, B3LYP.[78,79] The numerical integration in the XC part was done on an adaptive molecular grid and the rotational invariance of the results was preserved by means of a non-collinear approach with the spin density described by the norm of the spin magnetization vector.[80] The molecular grid was constructed as a superposition of atomic grids, each consisting of 40+10n radial grid points (where n is the period of a given element) and Lebedev's quadrature grid of adaptive size in the angular part.[81] All relativistic four-component results were obtained with the Dirac–Coulomb Hamiltonian imposing a restricted kinetic balance condition at the integral level to construct the small-component basis. The large-component basis, consisting of spherical Gaussians and used in the non-relativistic, X2C and four-component calculations, is discussed in the Results and Discussion section. The evaluation of the two-electron contributions to the Fock matrix is a dominant computational task, in particular for the four-component-based methodologies. To reduce the cost of this essential step, an *atom-pair approximation* for the electron repulsion integrals was used: the evaluation of four-center two-electron integrals over atom-centered small-component basis functions χ^{S} is discarded unless the bra and ket basis pairs share the same origin, i.e. $[\chi^{\mathrm{S}}_A\chi^{\mathrm{S}}_B|\chi^{\mathrm{S}}_C\chi^{\mathrm{S}}_D]\delta_{AB}\delta_{CD}$, where δ is the Kronecker delta function and A, B, C, and D refer to the origin of the basis functions. In all the relativistic calculations, nuclei were modelled by finite-sized Gaussian functions.[82] The change in energy gradient less than 10^{-7} was set as a SCF convergence threshold. The LvNED calculations used an external electric field with a cosine time dependence ($\cos \omega t$), in which the first period was enveloped by a linear function as suggested by Ding *et al.*[26] ($\frac{\omega t}{2\pi} \cos \omega t$). The use of the envelope ensures a more stable time evolution compared to using the cosine function only. The Euclidean norm of the difference between density matrices from two successive microiterations was chosen as the convergence criterion in LvNED and set to 10^{-6}. The frequencies and amplitudes of the external field as well as the setting of the time-domain calculations (such as time steps) will be discussed in the respective sections. Geometries of all systems are available in the Supporting Information.

5 Results and discussion

In this section, we present pilot applications of the two-component (X2C) and full four-component (4C) implementations of LvNED-DFT to the calculation of (hyper)polarizabilities of *p*-nitroaniline (*p*NA), CF_3X (X=Cl, Br, I) series, and the tungsten complex $[W(CO)_5py]$ (py = pyridine). *p*-nitroaniline was treated at the non-relativistic level of theory and was included in the test set in order to assess the current LvNED-DFT implementation against experiment and recent theoretical DFT results based on response theory. For the remaining systems, the newly developed relativistic methodology were used. It should be noted that there are several conventions used for reporting NLO properties, and this must be taken into account in order to avoid confusion when comparing results from different sources. Unless stated otherwise, we employ the so-called T convention of Willetts *et al.*[83]

5.1 *p*-nitroaniline

To assess the correctness of the non-relativistic LvNED implementation and the procedure for obtaining NLO properties, we applied the methodology to *p*-nitroaniline, an organic chromophore with a donor–(π-conjugated bridge)–acceptor structure exhibiting large first hyperpolarizabilities. The NLO properties of p-nitroaniline have been extensively studied in the past.[16,17,21,84,85]

We calculated the dynamical polarizabilities $\alpha(-\omega;\omega)$, the first hyperpolarizabilities $\beta(-2\omega;\omega,\omega)$ and $\beta(0;\omega,-\omega)$, and the second hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$ and $\bar{\gamma}(-\omega;\omega,\omega,-\omega)$ at the incident wavelength of 1064 nm (frequency 0.0428 a.u.), corresponding to a Nd:YAG laser. In the electron dynamics calculations we let the system evolve for 750 time steps of length 0.8 a.u. which corresponds to about 4 periods of the external harmonic field, including the linear envelope applied in the first period. The amplitude of the external field in Eqs. (28) and (29) was set to 0.002 a.u. All calculations were performed using Dunning's uncontracted aug-cc-pVDZ basis set.[86]

The results for pNA are summarized in Table 1 where we include only the tensor components needed for the calculation of rotationally averaged values. The benzene ring of the molecule was oriented in the xy plane, with x being the dipole axis. For this reason, α_{xx}, β_{xxx} and γ_{xxxx} dominate the overall NLO responses. For a given frequency and amplitude of the external field, response theory provides reliable reference values for the molecular (hyper)polarizabilities obtained from the electron dynamics simulations. The difference between the results of these two methods is indeed very small for the polarizability and the first hyperpolarizabilities – the differences are below 1%, with a few exceptions such as $\beta_{yxy}(0;\omega,-\omega)$ (2.3%). These small discrepancies can be partly attributed to implementational differences between the programs used (such as the program-specific DFT grids), but more importantly to the numerical procedure for extracting NLO properties by means of the finite difference evaluation and the least-square fitting of the induced electric dipole moment derivatives. The latter source of errors grows with the property order – for instance, the differences in the second hyperpolarizability components vary from 1% to almost 12% for $\gamma_{yyyy}(-3\omega;\omega,\omega,\omega)$. It turns out that the procedure exhibits even larger numerical inaccuracies for the off-diagonal components of γ when compared to the diagonal components, in particular when the former are evaluated at the $\mathcal{O}(A^2)$ precision for the numerical derivatives.

The dependence of the dominant diagonal components of the NLO property tensors on the precision of the numerical derivatives used in the electron dynamics simulations is summarized in Table 2. The precision $\mathscr{O}(A^2)$ seems to be sufficient for α and to some extent also for β, with the largest difference with respect to $\mathscr{O}(A^6)$ being 0.4% for $\beta_{xxx}^{\mathrm{SHG}}$, whereas for γ a significant improvement was achieved with the precision increased to $\mathscr{O}(A^4)$. In this case, the original difference of 4.2% between $\mathscr{O}(A^2)$ and $\mathscr{O}(A^6)$ for $\gamma_{xxxx}^{\mathrm{THG}}$ was reduced to 0.3%. In order to balance the accuracy and the computational cost (represented by the number of simulations) we applied the precision $\mathscr{O}(A^2)$ for α and β, and $\mathscr{O}(A^4)$ for γ.

In Table 1 we also report the experimentally accessible value for the averaged second harmonic generation coefficient $\beta_{||}$, as measured in the gas phase, $\beta_{||}^{\mathrm{exp}} = 2144.6$.[87] Even though the difference between the calculated and experimental values is almost 20%, the electron dynamics results are in agreement with response theory results reported by other groups; for instance, Sałek *et al.*[84] performed CCSD calculations on *p*NA ($\beta_{||}^{\mathrm{CCSD}} = 1600.1$) observing similar discrepancies and suggested that there might be a problem with the quality of the experimental data.

Table 1: Comparison of non-relativistic electron dynamics and response theory results for NLO properties (in atomic units) of *p*NA evaluated with B3LYP at the external field frequency $\omega = 0.0428\,\text{a.u.}$

Property		Electron dynamics[a]	Response theory
type	component		
$\alpha(-\omega;\omega)$	α_{xx}	168.0	167.9
	α_{yy}	104.3	104.3
	α_{zz}	55.8	55.8
$\beta(-2\omega;\omega,\omega)$	β_{xxx}	3171.5	3143.7
	β_{xyy}	-207.2	-203.0
	β_{xzz}	-88.1	-87.3
	β_{yxy}	-151.8	-154.4
	β_{zxz}	-80.4	-80.1
	$\beta_{\|\|}$[b,c]	1750.9	1734.3
$\beta(0;\omega,-\omega)$	β_{xxx}	2127.8	2095.4
	β_{xyy}	-136.9	-138.0
	β_{xzz}	-70.0	-69.9
	β_{yxy}	-144.8	-148.2
	β_{zxz}	-71.2	-71.3
$\gamma(-3\omega;\omega,\omega,\omega)$	γ_{xxxx}	931638	945089
	γ_{yyyy}	21169	18670
	γ_{zzzz}	14072	13900
$\bar{\gamma}(-\omega;\omega,\omega,-\omega)$	$\bar{\gamma}_{xxxx}$	181941	176035
	$\bar{\gamma}_{yyyy}$	13897	14419
	$\bar{\gamma}_{zzzz}$	11407	11406

[a] The numerical derivative precision used to calculate α and β was $\mathscr{O}(A^2)$, and $\mathscr{O}(A^4)$ for γ.

[b] $\beta_{||} = \frac{1}{5}\sum_i(\beta_{xii}+\beta_{ixi}+\beta_{iix})$

[c] $\beta_{||}^{\text{exp}} = 2144.59 \pm 87.51$[87]

Table 2: Dependence of the dominant diagonal components of NLO property tensors on the precision of the numerical derivatives used in the electron dynamics simulations. The non-relativistic NLO results (in atomic units) were evaluated for *p*NA at the external field frequency $\omega = 0.0428\,\mathrm{a.u.}$ and the number of simulations necessary to obtain the respective property component is reported in parentheses.

Property	Derivative precision in electron dynamics			Response Theory
	$\mathcal{O}(2)^a$	$\mathcal{O}(4)^b$	$\mathcal{O}(6)^c$	
$\alpha_{xx}(-\omega;\omega)$	168.09 (2)	167.99 (4)	167.99 (6)	167.87
$\beta_{xxx}(-2\omega;\omega,\omega)$	3171.46 (2)	3158.87 (4)	3158.25 (6)	3143.68
$\beta_{xxx}(0;\omega,-\omega)$	2128.36 (2)	2126.64 (4)	2126.72 (6)	2095.39
$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$	895251.49 (4)	931638.37 (6)	934507.56 (8)	945089.48
$\bar{\gamma}_{xxxx}(-\omega;\omega,\omega,-\omega)$	183471.61 (4)	181941.79 (6)	181887.06 (8)	176035.30

[a] Calculated using Eqs. (28)
[b] Calculated using Eqs. (29)
[c] Calculated using equations from the Supporting Information.

5.2 CF$_3$X (X = Cl, Br, I) series

In order to benchmark the newly developed two-component X2C-LvNED code, we calculated the SHG coefficents of the CF$_3$X (X=Cl, Br, I) series and the results were compared to the four-component response theory calculations recently reported by Bast *et al.*[88] The SHG coefficients $\beta(-2\omega;\omega,\omega)$ obtained from the electron dynamics simulations were evaluated at an incident harmonic field wavelength of 1064 nm (frequency 0.0428 a.u.) and with the amplitude of the external electric field of 0.002 a.u.. The system was evolved for 750 time steps of length 0.8 a.u. (about 4 periods of the external harmonic field, including the initial period with an envelope). The molecular orientation, geometries, and basis sets (the uncontracted triple-augmented cc-pVTZ basis sets for C, F, Cl, and Br, and Sadlej's polarization basis set for I), were chosen to be consistent with the work of Bast *et al.*.[88]

The results for the SHG coefficients of the CF$_3$X series are summarized in Table 3. The data show an overall excellent agreement between all three computational methods used. The differences between the 4C electron dynamics and response theory results are all below 1.5% and can be primarily attributed to same numerical aspects discussed in the previous section. On the other hand, the discrepancy between the NLO results obtained with the X2C and 4C electron dynamics, when performed within the same program suite/setup, is even smaller (below 0.5%) and the difference increases slightly when going from the light CF_3Cl to the heaviest analogue, CF_3I. Due to the approximative nature of the quasirelativistic X2C Hamiltonian, this observed trend is expected because of the increasing importance of relativistic effects along the series. Nevertheless, our X2C results clearly indicate that the theoretical assumptions – the adiabatic approximation and disregarding the picture-change transformation of the two-electron interactions – remain valid and the results obtained with these approximations are in excellent agreement with the reference 4C values. Moreover, the required simulation time for the X2C-LvNED was reduced by at least a factor of 7.1 compared to the full 4C scheme, and this factor increases even further for CF_3Br and CF_3I, as can be seen from Table 3.

To provide a deeper insight into the origin of the acceleration achieved by the X2C approach, we report in Table 4 the wall-clock time of individual computational tasks performed in one microiteration of a single electron dynamics time step. Whereas the exchange-correlation contribution (`xc`) is by far the least expensive task, for which the CPU time does not change with methodology, both the two-electron Fock matrix contribution (`eri`) and the propagator evaluation (`diag`) constitute a significant portion of the overall computational time and are therefore responsible for the observed acceleration of the X2C-LvNED. Furthermore, the acceleration in `eri` is more than sevenfold and almost constant throughout the series while the `diag` step exhibits more than eightfold speedup. Therefore, we expect that the two-component dynamics would result in acceleration by a factor of seven for systems dominated by the Fock matrix construction and more than eight for systems bound by the diagonalization step.

To conclude, the results support the use of X2C-LvNED both in terms of accuracy (agreement with the fully relativistic 4C method) as well as efficiency (the achieved speedup). In the next section we exploit these benefits in the calculation of optical properties of a larger, 6th row element containing system. At the same time, more tests for different molecular properties and spectroscopies are currently under way in our group.

Table 3: Comparison of relativistic X2C and 4C electron dynamics results with 4C response theory (RT) data for the polarizabilities $\alpha(-\omega;\omega)$ and second harmonic generation coefficients $\beta(-2\omega;\omega,\omega)$ of CF_3X (X = Cl, Br, I). The properties are presented in atomic units and evaluated with the B3LYP functional at the external field frequency $\omega = 0.0428\,\text{a.u.}$. An average wall-clock time (in seconds) along with the number of microiterations (in parentheses) per time step are also reported for electron dynamics simulations.[a]

Molecule	Property[b]		Electron dynamics		RT[c]	Wall-clock time[d]	
	type	component	X2C	4C	4C	X2C	4C
CF_3Cl	$\alpha(-\omega;\omega)$	α_{xx}	29.84	29.83	29.83		
		α_{zz}	38.43	38.43	38.43		
		α^e	32.70	32.70	32.70		
	$\beta(-2\omega;\omega,\omega)$	β_{zxx}	33.73	33.73	33.56		
		β_{xzx}	33.61	33.61	33.33		
		β_{zzz}	65.84	65.82	66.57		
		$\beta_{\vert\vert}{}^f$	79.88	79.87	80.03	46 (3.1)	328 (3.1)
CF_3Br	$\alpha(-\omega;\omega)$	α_{xx}	36.05	36.04	36.04		
		α_{zz}	49.05	49.04	49.04		
		α^e	40.38	40.37	40.37		
	$\beta(-2\omega;\omega,\omega)$	β_{zxx}	62.26	62.18	61.38		
		β_{xzx}	61.60	61.54	60.80		
		β_{zzz}	148.8	148.7	147.9		
		$\beta_{\vert\vert}{}^f$	163.5	163.3	161.9	65 (3.4)	500 (3.5)
CF_3I	$\alpha(-\omega;\omega)$	α_{xx}	47.13	47.10	47.09		
		α_{zz}	65.48	65.45	65.44		
		α^e	53.25	53.22	53.21		
	$\beta(-2\omega;\omega,\omega)$	β_{zxx}	114.1	113.7	113.2		
		β_{xzx}	110.6	110.1	110.3		
		β_{zzz}	302.8	302.0	305.4		
		$\beta_{\vert\vert}{}^f$	315.8	314.7	316.8	80 (4.2)	614 (4.1)

[a] The averaging performed over 750 time steps from simulations with an external field applied along the z direction.

[b] The numerical derivative precision was $\mathcal{O}(A^2)$.

[c] Polarizabilities were calculated using the linear response theory implementation in the `ReSpect` program; first hyperpolarizabilities were taken from the work of Bast *et al.*[88]

[d] The calculations performed on two compute nodes each equipped with 2.80 GHz Intel Xeon E5-2860 processor with 20 CPU-cores. The computer program `ReSpect` was compiled with Intel ifort 13.0 at -O3 level and linked against sequential Intel MKL library. The Message Passing Interface (MPI) implementation in OpenMPI 1.6.2 was used for parallel execution.

[e] $\alpha = \frac{1}{3}\sum_i \alpha_{ii}$. Due to symmetry, $\alpha_{xx} = \alpha_{yy}$.

[f] $\beta_{||} = \frac{1}{5}\sum_i(\beta_{zii} + \beta_{izi} + \beta_{iiz})$. Due to symmetry, $\beta_{xzx} = \beta_{xxz} = \beta_{yyz} = \beta_{yzy}$.

Table 4: Wall-clock time per microiteration (in seconds) for various computational tasks in relativistic electron dynamics simulations and speedup achieved by going from 4C to X2C Hamiltonians.[a]

Molecule	Task	Electron dynamics		Speedup
		4C	X2C	
CF_3Cl	`xc`[b]	3.4	3.3	1.0
	`eri`[c]	57.6	8.1	7.1
	`diag`[d]	21.8	2.5	8.7
	total	**105.8**	**14.8**	**7.1**
CF_3Br	`xc`[b]	3.4	3.4	1.0
	`eri`[c]	76.3	10.7	7.1
	`diag`[d]	30.3	3.4	8.9
	total	**142.9**	**19.1**	**7.5**
CF_3I	`xc`[b]	3.5	3.4	1.0
	`eri`[c]	77.7	10.5	7.4
	`diag`[d]	29.9	3.5	8.5
	total	**149.8**	**19.0**	**7.9**

[a] The calculations performed on two compute nodes each equipped with 2.80 GHz Intel Xeon E5-2860 processor with 20 CPU-cores. The computer program `ReSpect` was compiled with Intel ifort 13.0 at -O3 level and linked against sequential Intel MKL library. The Message Passing Interface (MPI) implementation in OpenMPI 1.6.2 was used for parallel execution.

[b] DFT non-collinear exchange-correlation contribution.

[c] Two-electron Fock matrix contribution.

[d] Fock matrix diagonalization in the propagator matrix construction.

5.3 [W(CO)$_5$py] complex

The last system considered was the pentacarbonyl-pyridine tungsten complex, a molecule containing an element from the 6th period for which significant relativistic contributions can be expected and which has been suggested to have a large first hyperpolarizability.[6] The complex was treated with X2C-LvNED at the DFT (B3LYP) level of theory with additional non-relativistic B3LYP and HF calculations performed in order to assess the importance of relativistic effects and electron correlation.

The optical properties of the complex were evaluated at the external electric field wavelength of 1908 nm (frequency 0.0239 a.u.), corresponding to a thulium laser and with the amplitude of

0.002 a.u.. The system was evolved for 7000 time steps of length 0.15 a.u. (about 4 periods of the external harmonic field, including the initial period with an envelope). The molecular orientation was chosen such that the dipole moment was aligned along the x axis. Dyall's uncontracted valence DZ basis set[89] was used for the tungsten atom, and uncontracted aug-cc-pVDZ basis for the remaining elements.[86]

The results obtained are summarized in Table 5. The non-relativistic B3LYP results for the polarizability are very close to the relativistic X2C values with less than 3.5% difference. Even the Hartree–Fock method offers a good estimate for the polarizability. This is no longer the case for the first hyperpolarizability. The dominant xxx component of the SHG tensor is one order of magnitude larger than other components, and it is also most influenced by both electron correlation and relativity. Not surprisingly, correlation effects are significant and are responsible for an order of magnitude change in this component (as well as in the experimentally accessible rotationally averaged $\beta_{||}$). Similarly, other components of the SHG are also significantly affected by electron correlation. The inclusion of relativistic effects causes another shift of about 35%, demonstrating the importance of relativity even for electric properties. These numbers indicate that for heavy-element containing systems the adequate inclusion of relativistic corrections is important in order to correctly describe higher-order response properties.

Table 5: Comparison of relativistic (X2C) and non-relativistic electron dynamics results for optical properties (in atomic units) of [W(CO)$_5$py] evaluated with B3LYP and HF at the external field frequency $\omega = 0.0239\,\text{a.u.}$.[a]

Property		Relativistic	Non-relativistic	
type	component	B3LYP	B3LYP	HF
$\alpha(-\omega;\omega)$	α_{xx}	235.3	227.5	197.9
	α_{yy}	198.3	195.2	183.0
	α_{zz}	181.3	178.0	166.0
$\beta(-2\omega;\omega,\omega)$	β_{xxx}	-4122.9	-3026.6	-347.2
	β_{xyy}	-102.4	-105.7	-148.8
	β_{xzz}	-113.6	-120.2	-178.5
	β_{yxy}	-115.3	-115.8	-153.8
	β_{zxz}	-125.7	-127.9	-178.0
	$\beta_{\|\|}$[b]	-2613.3	-1958.6	-406.5
$\beta(0;\omega,-\omega)$	β_{xxx}	-3359.9	-2537.5	-296.8
	β_{xyy}	-100.0	-108.8	-130.5
	β_{xzz}	-111.4	-122.5	-157.7
	β_{yxy}	-106.3	-108.5	-146.0
	β_{zxz}	-117.6	-121.3	-172.1

[a] The numerical derivative precision was $\mathcal{O}(A^2)$.

[b] $\beta_{||} = \frac{1}{5}\sum_i(\beta_{xii} + \beta_{ixi} + \beta_{iix})$.

6 Summary and outlook

We have presented the theory, implementation and pilot applications of relativistic electron dynamics based on the X2C-transformed Liouville–von Neumann equation. By means of an adiabatic approximation and the X2C transformation of the time-dependent Fock operator, we achieve a decoupling of the original four-component equation of motion (EOM) to the positive-energy and negative-energy branches. The upper two components then constitute the EOM "for the electrons only" and can be used to significantly accelerate the relativistic real-time dynamics, without the loss of accuracy in reproducing the relativistic scalar and spin–orbit effects. This leads to overall speed-up of the calculations by a factor of seven or more. Because the method is formulated entirely using matrix algebra, there is no need to generate explicit operator expressions for the higher-order relativistic corrections, as it is required for other two-component Hamiltonians such as ZORA or DKH/BSS. Furthermore, the picture-change transformation of the property operators can be done in a single step.

The method has been implemented at the Kohn–Sham DFT level of theory exploiting the noncollinear two- and four-component Kramers unrestricted formalism available in the program `ReSpect`. The calculations of molecular polarizabilities as well as first and second hyperpolarizabilities, extracted from time-dependent induced dipole moments using the finite-field method developed by Ding *et al.*,[26] have been used to assess the accuracy and performance of the proposed X2C Liouville–von Neumann electron dynamics (X2C-LvNED). The excellent agreement between the full four-component and the two-component treatment suggests that relativistic electron dynamics based on the X2C transformation may, at least for simulations involving electric fields as external perturbations, represent an exciting perspective in relativistic quantum chemistry, in particular when combined with a transition dipole decomposition and the Padé approximants-based technique of Bruner *et al.*[90] The X2C transformation is fully compatible with the calculation of electron absorption or XANES spectra – applications of the LvNED that we have previously presented at the four-component level of theory.[34,42] Further possibilities offered by the methodology, in particular for spectral techniques involving spin and external magnetic fields, are currently pursued in our laboratory, as it is known that the relativistic corrections for magnetic properties play an even more important role than for electric properties. During the revision process, a publication describing the development of X2C Hamiltonian-based electron dynamics and its application to the evaluation of UV/VIS spectra was published by Goings *et al.*[91]

Acknowledgement

This work has received support from the Slovak Research and Development Agency (grants APVV-0510-12 and APVV-15-0726) and the Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Sciences VEGA (grant No. 2/0148/13). LK acknowledges the National Scholarship Programme of the Slovak Republic (NSP). Support from the Research Council of Norway (Grants No 179568 and 214095) as well as from the European Research Council through a Starting Grant (No 279619) is also gratefully acknowledged. Computational time has been provided through a grant from the Norwegian supercomputing program NOTUR (Grant No NN4654K). MR gratefully acknowledges fruitful discussions with Professor Trond Saue on the X2C transformation.

7 Supporting Information

Molecular geometries of p-nitroaniline, CF_3X (X = Cl, Br, I), and $[W(CO)_5py]$. Formulas for the numerical derivatives of induced dipole moments with $\mathcal{O}(A^6)$ precision. This information is available free of charge via the Internet at http://pubs.acs.org/.

References

(1) Boyd, R. W. *Nonlinear Optics*; Academic Press, 2008; pp 1–67.

(2) Kanis, D. R.; Ratner, M. a.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195–242.

(3) Marder, S. R. *Chem. Commun.* **2006**, 131–134.

(4) Nakano, M.; Champagne, B. *J. Phys. Chem. Lett.* **2015**, *6*, 3236–3256.

(5) Masayoshi Nakano, B. C. *WIREs Comput. Mol. Sci.* **2016**, *6*, 198–210.

(6) Long, N. J. *Angew. Chem. Int. Ed.* **1995**, *34*, 21–38.

(7) Bella, S. *Chem. Soc. Rev.* **2001**, *30*, 355–366.

(8) Fukui, H.; Inoue, Y.; Yamada, T.; Ito, S.; Shigeta, Y.; Kishi, R.; Champagne, B.; Nakano, M. *J. Phys. Chem. A* **2012**, *116*, 5501–5509.

(9) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34–S39.

(10) Pople, J. A.; McIver, J. W.; Ostlund, N. S. *J. Chem. Phys.* **1968**, *49*, 2960–2964.

(11) Pulay, P. *J. Chem. Phys.* **1983**, *78*, 5043–5051.

(12) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910–1918.

(13) Maurice, D.; Head-Gordon, M. *Mol. Phys.* **1999**, *96*, 1533–1541.

(14) Olsen, J.; Jorgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235–3264.

(15) Christiansen, O.; Jorgensen, P.; Hattig, C. *Int. J. Quantum Chem.* **1998**, *68*, 1–52.

(16) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1998**, *109*, 10644–10656.

(17) Sałek, P.; Vahtras, O.; Helgaker, T.; Ågren, H. *J. Chem. Phys.* **2002**, *117*, 9630.

(18) Bast, R.; Ekström, U.; Gao, B.; Helgaker, T.; Ruud, K.; Thorvaldsen, A. J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2651.

(19) Helgaker, T.; Coriani, S.; Jorgensen, P.; Kristensen, K.; Olsen, J.; Ruud, K. *Chem. Rev.* **2012**, *112*, 543–631.

(20) Norman, P.; Bishop, D. M.; Jo/rgen Aa. Jensen, H.; Oddershede, J. *J. Chem. Phys.* **2001**, *115*, 10323–10334.

(21) Norman, P.; Bishop, D. M.; Jensen, H. J. A.; Oddershede, J. *J. Chem. Phys.* **2005**, *123*, 194103.

(22) Takimoto, Y.; Vila, F. D.; Rehr, J. J. *J. Chem. Phys.* **2007**, *127*, 154114.

(23) Wang, F.; Yam, C. Y.; Chen, G. *J. Chem. Phys.* **2007**, *126*, 244102.

(24) Liu, J.; Guo, Z.; Sun, J.; Liang, W. *Front. Chem. China* **2010**, *5*, 11–28.

(25) Goncharov, V. A.; Varga, K. *J. Chem. Phys.* **2012**, *137*, 094111.

(26) Ding, F.; Van Kuiken, B. E.; Eichinger, B. E.; Li, X. *J. Chem. Phys.* **2013**, *138*, 064104.

(27) Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C. A.; Andrade, X.; Lorenzen, F.; Marques, M. A.; Gross, E.; Rubio, A. *Phys. Status Solidi B* **2006**, *243*, 2465–2488.

(28) Theilhaber, J. *Phys. Rev.* **B 1992**, *46*, 12990.

(29) Yabana, K.; Bertsch, G. *Phys. Rev.* **B 1996**, *54*, 4484.

(30) Tsolakidis, A.; Sánchez-Portal, D.; Martin, R. *Phys. Rev.* **B 2002**, *66*, 235416.

(31) Baer, R.; Neuhauser, D. *J. Chem. Phys.* **2004**, *121*, 9803–9807.

(32) Yabana, K.; Nakatsukasa, T.; Iwata, J.-I.; Bertsch, G. F. *Phys. Status Solidi B* **2006**, *243*, 1121–1138.

(33) Lopata, K.; Govind, N. *J. Chem. Theory Comput.* **2011**, *7*, 1344–1355.

(34) Repisky, M.; Konecny, L.; Kadek, M.; Komorovsky, S.; Malkin, O. L.; Malkin, V. G.; Ruud, K. *J. Chem. Theory Comput.* **2015**, *11*, 980–991.

(35) Isborn, C. M.; Li, X. *J. Chem. Phys.* **2008**, *129*, 204107.

(36) Isborn, C. M.; Li, X. *J. Chem. Theory Comput.* **2009**, *5*, 2415–2419.

(37) Cheng, C.-L.; Evans, J. S.; Van Voorhis, T. *Phys. Rev.* **B 2006**, *74*, 155112.

(38) Goings, J. J.; Li, X. *J. Chem. Phys.* **2016**, *144*.

(39) Lee, K.-M.; Yabana, K.; Bertsch, G. *J. Chem. Phys.* **2011**, *134*, 144106.

(40) Akama, T.; Imamura, Y.; Nakai, H. *Chem. Lett.* **2010**, *39*, 407–409.

(41) Lopata, K.; Van Kuiken, B. E.; Khalil, M.; Govind, N. *J. Chem. Theory Comput.* **2012**, *8*, 3284–3292.

(42) Kadek, M.; Konecny, L.; Gao, B.; Repisky, M.; Ruud, K. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22566–22570.

(43) Lestrange, P. J.; Nguyen, P. D.; Li, X. *J. Chem. Theory Comput.* **2015**, *11*, 2994–2999.

(44) Fischer, S. A.; Cramer, C. J.; Govind, N. *J. Chem. Theory Comput.* **2015**, *11*, 4294–4303.

(45) Gao, B.; Ruud, K.; Luo, Y. *J. Chem. Phys.* **2012**, *137*, 194307.

(46) Dirac, P. *Proc. R. Soc. London Ser. A* **1928**, *117*, 610–624.

(47) Dirac, P. *Proc. R. Soc. London Ser. A* **1928**, *118*, 351–361.

(48) Breit, G. *Phys. Rev.* **1929**, *34*, 553–573.

(49) Gaunt, J. *Proc. R. Soc. London Ser. A* **1929**, *122*, 513–532.

(50) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89–155.

(51) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756–763.

(52) Wolf, A.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2002**, *117*, 9215–9226.

(53) Chang, C.; Pelissier, M.; Durand, P. *Phys. Scr.* **1986**, *34*, 394–404.

(54) Lenthe, E. V.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597–4610.

(55) Dyall, K. G. *J. Chem. Phys.* **1997**, *106*, 9618–9628.

(56) Cremer, D.; Zou, W.; Filatov, M. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2014**, *4*, 436–467.

(57) Heully, J. L.; Lindgren, I.; Lindroth, E.; Lundqvist, S.; Martensson-Pendrill, A. M. *J. Phys. B: At. Mol. Phys.* **1986**, *19*, 2799–2815.

(58) Jensen, H. J. A. "Douglas–Kroll the Easy Way", The Conference Talk, REHE 2005, Mülheim (Germany).

(59) Kutzelnigg, W.; Liu, W. *J. Chem. Phys.* **2005**, *123*, 241102.

(60) Liu, W.; Kutzelnigg, W. *J. Chem. Phys.* **2007**, *126*, 114107.

(61) Iliaš, M.; Saue, T. *J. Chem. Phys.* **2007**, *126*, 064102.

(62) Filatov, M. *J. Chem. Phys.* **2006**, *125*, 107101.

(63) Heß, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. *Chem. Phys. Lett.* **1996**, *251*, 365–371.

(64) Peng, D.; Liu, W.; Xiao, Y.; Cheng, L. *J. Chem. Phys.* **2007**, *127*, 104106.

(65) Sikkema, J.; Visscher, L.; Saue, T.; Iliaš, M. *J. Chem. Phys.* **2009**, *131*, 124116.

(66) Peng, D.; Reiher, M. *J. Chem. Phys.* **2012**, *136*, 244108.

(67) Kutzelnigg, W. *J. Chem. Phys.* **1999**, *110*, 8283–8294.

(68) Kosloff, R. *J. Phys. Chem.* **1988**, *92*, 2087–2100.

(69) Castro, A.; Marques, M. a. L.; Rubio, A. *J. Chem. Phys.* **2004**, *121*, 3425–33.

(70) Magnus, W. *Comm. Pure Appl. Math.* **1954**, *7*, 649–673.

(71) **ReSpect**, version 3.5.0, 2016 – Relativistic Spectroscopy DFT Program of Authors: Repisky M.; Komorovsky S.; Malkin V. G.; Malkina O. L.; Kaupp M.; Ruud K., with contributions from Bast R.; Ekstrom U.; Kadek M.; Knecht S.; Konecny L.; Malkin Ondik I.; Malkin E. See www.respectprogram.org, (accessed Sep 12, 2016).

(72) Stanton, R. E.; Havriliak, S. *J. Chem. Phys.* **1984**, *81*, 1910–1918.

(73) Peng, D.; Middendorf, N.; Weigend, F.; Reiher, M. *J. Chem. Phys.* **2013**, *138*, 184105.

(74) Fornberg, B. *Math. Comp.* **1988**, *51*, 699–699.

(75) Jones, E.; Oliphant, T.; Pearu, P. SciPy: Open source scientific tools for Python. 2001–; "`http://www.scipy.org/`", (accessed Sep 12, 2016).

(76) **Dalton**, a molecular electronic structure program, Release Dalton2015.1 (2015) See http://daltonprogram.org, (accessed Sep 12, 2016).

(77) Aidas, K.; Angeli, C.; Bak, K. L.; Bakken, V.; Bast, R.; Boman, L.; Christiansen, O.; Cimiraglia, R.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Ekström, U.; Enevoldsen, T.; Eriksen, J. J.; Ettenhuber, P.; Fernández, B.; Ferrighi, L.; Fliegl, H.; Frediani, L.; Hald, K.; Halkier, A.; Hättig, C.; Heiberg, H.; Helgaker, T.; Hennum, A. C.; Hettema, H.; Hjertenæs, E.; Høst, S.; Høyvik, I.-M.; Iozzi, M. F.; Jansík, B.; Jensen, H. J. Aa.; Jonsson, D.; Jørgensen, P.; Kauczor, J.; Kirpekar, S.; Kjærgaard, T.; Klopper, W.; Knecht, S.; Kobayashi, R.; Koch, H.; Kongsted, J.; Krapp, A.; Kristensen, K.; Ligabue, A.; Lutnæs, O. B.; Melo, J. I.; Mikkelsen, K. V.; Myhre, R. H.; Neiss, C.; Nielsen, C. B.; Norman, P.; Olsen, J.; Olsen, J. M. H.; Osted, A.; Packer, M. J.; Pawlowski, F.; Pedersen, T. B.; Provasi, P. F.; Reine, S.; Rinkevicius, Z.; Ruden, T. A.; Ruud, K.; Rybkin, V. V.; Sałek, P.; Samson, C. C. M.; de Merás, A. S.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sneskov, K.; Steindal, A. H.; Sylvester-Hvid, K. O.; Taylor, P. R.; Teale, A. M.; Tellgren, E. I.; Tew, D. P.; Thorvaldsen, A. J.; Thøgersen, L.; Vahtras, O.; Watson, M. A.; Wilson, D. J. D.; Ziolkowski, M.; Ågren, H. *WIREs Comput. Mol. Sci.* **2015**, *4*, 269–284.

(78) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(79) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **B 1988**, *37*, 785.

(80) van Wüllen, C. *J. Comput. Chem.* **2002**, *23*, 779–785.

(81) Krack, M.; Köster, A. M. *J. Chem. Phys.* **1998**, *108*, 3226–3234.

(82) Visscher, L.; Dyall, K. G. *At. Data Nucl. Data Tables* **1997**, *67*, 207–224.

(83) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(84) Sałek, P.; Helgaker, T.; Vahtras, O.; Ågren, H.; Jonsson, D.; Gauss, J. *Mol. Phys.* **2005**, *103*, 439–450.

(85) Day, P. N.; Pachter, R.; Nguyen, K. a. *J. Chem. Phys.* **2014**, *140*, 184308.

(86) Kendall, R. A.; Dunning Jr, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(87) Kaatz, P.; Donley, E. A.; Shelton, D. P. *J. Chem. Phys.* **1998**, *108*, 849.

(88) Bast, R.; Saue, T.; Henriksson, J.; Norman, P. *J. Chem. Phys.* **2009**, *130*, 024109.

(89) Dyall, K. G.; Gomes, A. S. P. *Theor. Chem. Acc.* **2010**, *125*, 97–100.

(90) Bruner, A.; LaMaster, D.; Lopata, K. *J. Chem. Theory Comput.* **2016**, *12*, 3741–3750.

(91) Goings, J. J.; Kasper, J. M.; Egidi, F.; Sun, S.; Li, X. *J. Chem. Phys.* **2016**, *145*, 104107.

Figure 1: For Table of Contents Only