The ab initio calculation of molecular electric, magnetic and geometric properties

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We give an account of some recent advances in the development of ab initio methods for the calculation of molecular response properties, involving electric, magnetic, and geometric perturbations. Particular attention is given to properties in which the basis functions depend explicitly both on time and on the applied perturbations such as perturbations involving nuclear displacements or external magnetic fields when London atomic orbitals are used. We summarize a general framework based on the quasienergy for the calculation of arbitrary-order molecular properties using the elements of the density matrix in the atomic-orbital basis as the basic variables. We demonstrate that the necessary perturbed density matrices of arbitrary order can be determined from a set of linear equations that have the same formal structure as the set of linear equations encountered when determining the linear response equations (or time-dependent self-consistent-field equations). Additional components needed to calculate properties involving perturbation-dependent basis sets are flexible one- and two-electron integral techniques for geometric or magnetic-field differentiated integrals; in Kohn–Sham density-functional theory (KS-DFT), we also need to calculate derivatives of the exchange–correlation functional. We describe a recent proposal for evaluating these contributions based on automatic differentiation. Within this framework, it is now possible to calculate any molecular property for an arbitrary self-consistent-field reference state, including two- and four-component relativistic self-consistent-field wave functions. Examples of calculations that can be performed with this formulation are presented.

1. Introduction

There has in recent years been an increasing interest in nonlinear optical spectroscopies, theoretically as well as experimentally.1 These developments have been driven by the advent of new lasers in different frequency regions, from the infrared
to the ultraviolet region of the electromagnetic spectrum, making highly sophisticated nonlinear experiments not only possible but often also routine. Examples of such nonlinear spectroscopies include coherent anti-Stokes Raman scattering,\textsuperscript{2, 6} Jones birefringence,\textsuperscript{7, 8} magnetic-field-induced birefringence,\textsuperscript{9, 10} two-photon absorption,\textsuperscript{11, 12} two-photon circular dichroism,\textsuperscript{13} and doubly vibrationally enhanced infrared four-wave mixing,\textsuperscript{14} to mention but a few of the many properties that can arise at high orders. Many papers report on the possible novel applications that nonlinear spectroscopies may facilitate, ranging from three-dimensional data storage\textsuperscript{15–17} to photodynamic therapy\textsuperscript{18} and multifunctional materials,\textsuperscript{19, 20} including molecular switches.\textsuperscript{21, 22}

Increasing computer power combined with improvements in the algorithms used to calculate molecular properties has led to a growth in the number of computational studies of molecular properties. The determination of molecular first and second geometric derivatives has for a long time been well established\textsuperscript{23, 24} due to the interest in optimizing molecular structures and determining molecular force fields. In recent years, there has also been a large growth in theoretical implementations of other first- and second-order molecular properties such as shielding constants and indirect spin–spin coupling constants of nuclear magnetic resonance (NMR) spectroscopy,\textsuperscript{25–29} chiroptical properties such as optical rotation and electronic circular dichroism,\textsuperscript{30–32} as well as properties related to open-shell species such as hyperfine interactions and electronic g tensors.\textsuperscript{26, 33}

Likewise, in the field of higher-order molecular properties, there has been an increasing interest in the \textit{ab initio} calculation of properties such as the first and second hyperpolarizabilities,\textsuperscript{1} magnetic circular dichroism and Verdet constants,\textsuperscript{34–38} various Raman- and hyper-Raman-related properties,\textsuperscript{39–46} as well as a number of fourth-order birefringences.\textsuperscript{7, 8} However, most of these developments have focused on perturbations involving one-electron operators only. In practice, most of these studies have therefore focused on properties arising from an external electric field. However, many higher-order molecular responses involve perturbations for which the atomic-orbital (AO) basis set has an explicit

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dependence on the applied perturbation. The most obvious examples of such perturbations are properties related to vibrational spectroscopies, which depend on the forces and force fields. Since it is common practice in molecular electronic-structure calculations to fix the AO basis functions to the atomic centers, the basis set changes when these centers are displaced.\textsuperscript{23,24} Other examples are molecular magnetic properties calculated using London atomic orbitals (LAOs),\textsuperscript{27–40} with an explicit field dependence. We also note that similar electric-field dependent basis functions have been introduced\textsuperscript{40,51} but have received less attention than the nuclear and magnetic-field dependent orbitals. We refer to such basis sets as perturbation-dependent basis sets (PDBSs).

A consequence of the dependence of AOs on the applied perturbations is that the formalism for the calculation of molecular properties contains, in addition to contributions arising from interactions in the Hamiltonian operator leading to perturbed densities, contributions from lower-order densities with corrections arising from derivatives of the AOs, giving rise to a large variety of new one- and two-electron integrals.\textsuperscript{52,53}

To calculate an arbitrary molecular property of any order for basis functions that may be time and perturbation dependent, the computational machinery must contain a number of independent components, all designed in a flexible manner. It is the purpose of this perspective to describe the various components that need to be available to calculate arbitrary molecular properties, building on the many developments previously presented in the literature, and to illustrate how such a flexible framework may allow for new and exciting molecular properties to be studied \textit{ab initio}. We focus on our own efforts in this field, describing recent advances made in our group in developing an open-ended response theory in the AO basis, an open-ended one- and two-electron integration scheme for arbitrary operators differentiated to arbitrary order, and an automatic differentiation scheme for exchange-correlation (XC) functionals to arbitrary order.

The remainder of the paper is organized as follows. First, in section 2, we give a historical overview of methods for calculating linear and nonlinear molecular properties. Next, in section 3, we describe our recent approaches for developing a flexible toolbox for arbitrary-order molecular properties. In section 4, we give some examples of our recent applications of the code. Section 5 contains concluding remarks and an outlook.

### 2. Historical overview

With the exception of some lower-order molecular properties, the development of computational approaches for molecular properties has progressed along two complementary and largely separate paths. On the one hand, response-theory approaches\textsuperscript{54} or quasienergy derivative techniques\textsuperscript{55–57} have been developed for frequency- (or time-) dependent molecular properties generated by one-electron perturbing operators; on the other hand, analytical derivative techniques\textsuperscript{58,59} have been developed for PDBSs to describe geometric perturbations (molecular forces and force fields) and magnetic perturbations (NMR shielding constants).

Most computer codes today provide routines for solving the linear Hartree–Fock (HF) and Kohn–Sham (KS) response equations that determine the first-order perturbed molecular-orbital coefficients in the presence of an external perturbation such as a (frequency-dependent) electric field. We do not attempt to review all these approaches here, referring the reader to the collected reviews in ref. \textsuperscript{1}. Instead, we focus on the more general and open-ended approaches presented in the literature, utilizing the recursive nature of the general perturbation-theory expressions.\textsuperscript{60,61}

#### 2.1 Response theory

The first open-ended approach for higher-order molecular properties of one-electron perturbing operators was that of Dykstra and Jasien\textsuperscript{62} based on energy-derivative theory for static (time-independent) perturbations. Shortly thereafter, Sekino and Bartlett presented an open-ended analytic approach for frequency-dependent HF (hyper)polarizabilities,\textsuperscript{63} based on Frenkel’s variation principle for the Schrödinger equation.\textsuperscript{64} A similar scheme for time-dependent HF theory was later presented by Karn and Dupuis.\textsuperscript{65}

In 1985, Jørgensen and Olsen presented a general framework for calculating molecular properties using response theory\textsuperscript{54} based on the Ehrenfest theorem,\textsuperscript{66} collecting corrections to the wave function at different orders in the perturbation and identifying these with molecular properties of different orders. An important aspect of their work was the introduction of a parametrization that allowed the general equations for exact states to be easily transferred to approximate states such as those of HF and multi-configurational self-consistent-field (MCSCF) theories. Moreover, their paper presented an analysis of response-function residues, identifying these with transition moments (or excited-state molecular properties). General implementations of linear,\textsuperscript{67,68} quadratic\textsuperscript{69,70} and cubic\textsuperscript{71} response functions were presented by Jørgensen, Ågren and coworkers for HF and MCSCF wave functions. More recently, this framework has been extended to KS-DFT.\textsuperscript{72–74} A generalization to coupled-cluster theory was presented by Koch and Jørgensen,\textsuperscript{75} building on the Lagrangian approach for non-variational methods developed by Helgaker and Jørgensen.\textsuperscript{76} An important element of this work were the $2n+1$ and $2n+2$ rules of non-variational wave functions, proved by Helgaker and Jørgensen in ref. \textsuperscript{58}.

An alternative theoretical approach to response properties is the quasienergy formalism, defining molecular properties as derivatives of the quasienergy, first discussed by Hayes and Parr,\textsuperscript{77} and later by Langhoff, Epstein and Karplus.\textsuperscript{55} An attractive feature of this approach is that it allows computational expressions for frequency-dependent properties to be derived using the methods of energy-derivative theory, thereby facilitating the derivation of the working equations for computer implementations. However, the quasienergy approach only started to gain popularity in the 1990s with the work of Aiga, Sasagane and Itoh,\textsuperscript{56} who showed that it also would allow for the calculation of response properties for non-variational wave functions when combined with the Lagrangian approach of Helgaker and Jørgensen.\textsuperscript{76,78} This approach was put into a general response-theory framework
by Christiansen, Jørgensen and Hättig, who demonstrated that transition moments can be derived from the quasienergy derivatives using a residue analysis analogous to that used for response functions. The approach of Christiansen et al. was used to derive an open-ended scheme for calculating arbitrary-order hyperpolarizabilities at the coupled-cluster singles-and-doubles (CCSD) level of theory. The quasienergy approach is now the most popular means of deriving response functions and forms the starting point for our approach, in which the quasienergy approach is extended to include corrections due to perturbation dependence in the basis set. However, we first give a brief account of the development of methods for calculating molecular properties using PDBSs, starting with static molecular properties, before considering frequency-dependent properties.

2.2 Geometric derivatives

Although the analytical expression for molecular gradients was first presented by Bratoz, Pulay was the first to recognize the power of analytic derivative methods for the calculation of molecular forces, expressing the molecular gradient for a HF wave function (with respect to nuclear coordinate $R_{KS}$) as an expectation-value contribution involving the forces acting on the nuclei, correction terms arising from the differentiated one- and two-electron integrals (and nuclear repulsion), $\partial E/\partial R_{KS}$, and a term involving the differentiated overlap matrix $\partial S/\partial R_{KS}$,

$$\frac{dE(D)}{dR_{KS}} = \frac{\partial E(D)}{\partial R_{KS}} - \text{Tr} \left( \frac{\partial S}{\partial R_{KS}} W \right), \quad (1)$$

where $E(D)$ is the molecular energy as a function of the AO density matrix $D$, and $W$ the so-called energy-weighted density matrix given by

$$W = D F D,$$  

where $F$ is the AO Fock matrix. The last term in eqn (1) is still often referred to as the Pulay force, and the corrections from the differentiated integrals and the Pulay force vanish in the limit of a complete one-electron basis, making the forces acting on the nuclei proportional to the electric field at the nuclei, in agreement with the Hellmann–Feynman theorem. In second quantization, a particularly convenient treatment of PDBSs is that given by Helgaker and Almlöf, where the effects of perturbation-dependent basis functions are absorbed in the electronic Hamiltonian. We shall revisit the expression in eqn (1) when discussing our approach for calculating response functions for time- and perturbation-dependent basis sets.

The molecular gradient technique pioneered by Pulay was subsequently generalized to other levels of theory such as second-order Moller–Plesset theory (MP2) by Pople et al. and configuration-interaction (CI) theory by Krishnan et al. and Brooks et al. A significant step forward was the efficient generalization to non-variational wave functions by the Handy–Schaefer Z-vector method in 1984, later generalized to the Lagrangian method. The first coupled-cluster analytical gradient was reported by Adamowicz, Lairdie and Bartlett in 1984, employing the Z-vector method.

Despite the added cost of calculating differentiated one- and two-electron integrals, significant improvements in computational efficiency are obtained when molecular gradients are calculated using analytical-derivative techniques rather than finite-difference methods. Even greater gains are observed when this approach is extended to higher derivatives such as molecular Hessians (force constants). Pople and coworkers were the first to introduce an efficient implementation of second derivatives at the HF and coupled-cluster doubles (CCD) level of theory, demonstrating the great advantages offered by analytic methods over finite-difference methods. Still, given the significant time and programming efforts needed to obtain analytical second derivatives, these were available only for MCSCF and MP2 theories at the end of the 1980s. The first implementation of analytic Hessians at the CCSD level of theory was presented by Koch et al. More efficient implementations of analytic force fields for non-variational methods were later developed by Gauss and Stanton. A review of the developments of analytic derivative methods for correlated methods has been given by Stanton and Gauss. With the increasing popularity of KS-DFT, an analytic scheme for calculating molecular force fields at the KS-DFT level was presented by Komornicki and Fitzgerald, as well as by Johnson and Frisch, and more recently by Degelnann, Fürche and Ahlrichs.

Analytic calculations of cubic and higher-order contributions to the molecular forces are very limited; indeed, we are only aware of the pioneering work of Handy and coworkers, who developed an analytic approach for calculating cubic and quartic force fields. They also presented a scheme for calculating the first and second geometric derivatives of the dipole moment and the electric polarizability. Despite the obvious advantages of such an analytic approach, the code has not been much used after the initial applications to for instance a study of the anharmonic force field of benzene.

2.3 Magnetic derivatives

Another area in which PDBSs have found much use is the field of magnetic properties. In approximate calculations of magnetic properties such as NMR shielding constants and magnetizabilities, the calculated quantities depend on an arbitrarily chosen gauge origin. By introducing an explicit dependence on the externally applied magnetic field $B$ by multiplying the conventional AOs by a field-dependent phase factor

$$\chi_k(r) = \exp \left[ -\frac{i}{2} B \cdot (R_k - G) \times (r - P) \right] \times \theta_k (r - R_k) \rho_k (|r - R_k|),$$ \quad (3)

gauge-origin independent results are obtained for variational methods even in finite basis sets, for non-variational methods such as coupled-cluster theory, origin independence is achieved for static fields. In eqn (3), $\chi_k$ is centered at the nuclear position $R_k$, $B$ is the magnetic field, $G$ is the gauge origin of the magnetic vector potential, and $P$ is the origin of the London phase factor $\exp \left[ -i B \cdot (R_k - G) \times (r - P) \right]$. The second factor $\theta_k(r_k)$ in eqn (3) is the angular part of the AO, typically a solid harmonic function $S_{\ell m}(r_k)$ in the
position \(r_k\) of the electron relative to the center of the AO. Finally, \(\rho_k(r_k)\) is a decaying radial form in \(r_k\), usually chosen as a contracted Gaussian

\[
\rho_k(r_k) = \sum_i w_{\alpha k} \exp(-a_{\alpha k} r_k^2),
\]

where \(w_{\alpha k}\) and \(a_{\alpha k}\) are the radial contraction coefficients and orbital exponents, respectively.

The orbitals \(\chi_k\) are known as gauge-including AOs (GIAOs) or London AOs after Fritz London, who introduced their use in 1937.\(^{47}\) Except for some early calculations of nuclear shielding constants by Ditchfield in the 1970s,\(^{108,109}\) the first efficient implementation was presented by Wolinski, Hinton and Pulay in 1990.\(^{48}\) Although several other schemes for solving the gauge-origin problem have been presented,\(^{110–117}\) the use of LAOs has proved to be the most successful, partly because LAOs allow us to build directly on the techniques of analytic derivative theory for nuclear displacements at all levels of electronic-structure theory, and partly because LAOs have been shown to be applicable to a large number of different molecular magnetic properties.

Restricting ourselves to static magnetic perturbations, most implementations of LAOs have focused on second-order properties—in particular, shielding constants at various level of theory. After the pioneering HF work by Wolinski \textit{et al.},\(^{48}\) implementations have been presented at the MP2,\(^{106,107}\) CCSD\(^{118}\) and coupled-cluster singles-doubles-perturbative-triples (CCSD(T))\(^{119}\) levels of theory, as well as for higher-order coupled-cluster theories\(^{120,121}\) up to the full-configuration interaction (FCI) limit.\(^{122}\) Implementations of NMR shielding constants using LAOs have also been presented at the MCSF level of theory\(^{123}\) and for KS-DFT.\(^{124}\) The \textit{ab initio} calculation of shielding constants is still an active field of research, but the review by Helgaker, Jaszunski and Ruud\(^{25}\) remains an up-to-date account of the methods in use for calculating NMR parameters. More recent reviews, including discussions of the importance of relativistic effects for NMR properties, can be found in ref. 27–29.

Apart from shieldings, LAOs have been used for the calculation of the magnetic-field analogue of the polarizability—namely, the magnetizability, which is the (negative) second magnetic-field derivative of the energy.\(^{125,126}\) Other uses of LAOs in connection with energy-derivative theory are for spin–rotation constants, observable from the hyperfine structure of rotational spectra, and for rotational \(g\) tensors, observable in microwave Zeeman experiments.\(^{127}\) To calculate these properties reliably, Gauss, Helgaker and Ruud introduced the concept of rotational LAOs, closely related to the LAOs, but with an explicit dependence on the rotational moment of the molecule rather than on the external field.\(^{128}\) Mixed magnetic-field and geometric derivatives have been calculated analytically using LAOs to obtain the atomic axial tensors that determine the rotatory strength in vibrational circular dichroism.\(^{129–131}\) We also note recent work in which LAOs have been used in a non-perturbative manner to study the behaviour of molecules in finite magnetic fields.\(^{132,133}\)

### 2.4 Frequency-dependent properties with PDBSs

With some notable exceptions, the theories for frequency-dependent molecular properties and for properties involving PDBS have developed separately. The earliest examples of combining time- and basis-set perturbation dependence are LAO-based gauge-origin independent approaches for calculating electronic circular dichroism\(^{134,135}\) and optical rotation.\(^{136–138}\) A key element for this development was the work of Helgaker and Jørgensen, who derived a second-quantized operator that incorporates all basis-set perturbation dependence into the Hamiltonian\(^{49}\) in analogy with geometric distortions,\(^{54}\) leading to a natural definition of an angular-momentum operator with the correct origin dependence for finite basis sets with LAOs.\(^{134,139}\)

A more unified treatment for handling frequency-dependent perturbations in connection with LAOs was proposed by Krykunov and Autschbach, who introduced time-periodic LAOs to treat such properties on an equal footing.\(^{140}\) This approach was utilized by these authors to calculate a variety of frequency-dependent properties involving static or frequency-dependent magnetic fields, such as Verdet constants,\(^{141}\) resonance Raman optical activity,\(^{141}\) optical rotation at resonant frequencies\(^{142}\) and the \(\beta\) term of magnetic circular dichroism (MCD).\(^{140}\) Similar implementations have been presented by Coriani, Jørgensen and coworkers for Verdet constants, for both coupled-cluster theory\(^{142}\) and linear-scaling KS-DFT.\(^{147}\)

Important contributions to the analytic calculation of higher-order molecular properties involving time- and PDBSs come from Champagne and coworkers, extending the work of Jayatilaka \textit{et al.}\(^{39}\) to frequency-dependent polarizabilities. Quinet and Champagne developed a coupled-perturbed HF scheme for calculating frequency-dependent polarizability gradients,\(^{40,41}\) Rappoport and Furetche have presented KS-DFT polarizability gradients,\(^{43}\) as a linear-scaling AO-basis formulation of KS-DFT polarizability gradients has been presented by Coriani \textit{et al.}\(^{38}\) Quinet and Champagne later extended their approach to the geometric second derivatives of the polarizability,\(^{142}\) and to the first- and second-order geometric derivatives of the first hyperpolarizability. Other interaction operators beyond the electric field were also considered by this group, such as the mixed electric dipole–electric quadrupole polarizability,\(^{144}\) and the mixed electric dipole–magnetic dipole polarizability, determining Raman Optical Activity spectra.\(^{44}\)

A property closely related to the properties involving both time- and perturbation-dependent basis sets that we have so far discussed is the excited-state gradient, important for determining excited-state geometries. As for polarizability gradients, several implementations at the KS-DFT level\(^{146–148}\) and coupled-cluster theory\(^{149,150}\) have been presented in the literature.

### 3. Theory

As we briefly reviewed in the previous section, a number of different approaches have been introduced for calculating a variety of molecular properties using time- and perturbation-dependent basis sets, largely at the self-consistent-field (SCF)
level of theory (i.e. HF and KS-DFT), but also in many cases at the correlated coupled-cluster level of theory. However, these implementations are still characterized by being targeted at specific orders, and almost without exceptions limited to the nonrelativistic level of theory. On this background, we have in recent years been much involved in the development of a unified computational framework for calculating molecular properties of arbitrary order with basis sets depending on time-dependent perturbations. The scheme has been developed for an arbitrary SCF method, and formulated fully in the AO basis. In this way, we may take advantage of recent advances made in the calculation of molecular properties using linear scaling techniques, as well as use a common framework for calculating molecular properties both at the non-relativistic level of theory as well as for two- and four-component relativistic wave functions. We now turn to a description of the toolbox that we have developed in order to meet our ambitions to provide a general and flexible framework for the calculation of arbitrary molecular properties.

### 3.1 A density-matrix-based quasienergy derivative theory for time- and perturbation-dependent basis sets

We will in this subsection introduce our approach for calculating molecular properties of arbitrary order for basis sets that are time and perturbation dependent. The formalism has recently been presented for the specific case of nonrelativistic HF and KS-DFT, as well as been extended to the four-component relativistic level. We will not repeat all the details here, but we will outline the main elements of the formalism with the purpose of illustrating how the approach allows us to identify the building blocks from which we can calculate any kind of molecular property for an arbitrary SCF reference state.

Let us consider a time-dependent molecular system described by the time-dependent Schrödinger (or Dirac) equation

\[
\hat{H}\psi = (\hat{H}_0 + \hat{V})\psi = i\frac{\partial \psi}{\partial t}
\]  

where the total Hamiltonian \(\hat{H}\) is written as the sum of a time-independent unperturbed Hamiltonian \(\hat{H}_0\) and a time-dependent operator \(\hat{V}\) representing the applied perturbations, and \(\psi\) is the time-dependent wave function describing the system. The exact form of the zeroth-order Hamiltonian \(\hat{H}_0\) is not important at this stage, and can be either a non-relativistic or relativistic Hamiltonian, and we assume only that it depends nonlinearly on the one-electron density matrix.

The perturbation operator is Hermitian and is a series of products of time-dependent perturbation strengths \(\varepsilon_A(t)\) and time-independent perturbing operators \(\hat{A}\).

\[
\hat{V} = \varepsilon_A(t)\hat{A} + \varepsilon_B(t)\hat{B} + \varepsilon_C(t)\hat{C} + \cdots \tag{6}
\]

For instance, choosing the perturbation to be external homogeneous electric and magnetic fields, the perturbation operator would be

\[
\hat{V} = F(t)(-\hat{\mu}_{el}) + B(t)(-\hat{\mu}_{mag}) \tag{7}
\]

where \(F(t), B(t), \hat{\mu}_{el}\) and \(\hat{\mu}_{mag}\) are the electric and magnetic-field vectors and dipole moment operators, respectively (we note the conventional opposite sign for the potential and moment operators).

We write the perturbation strengths in eqn (6) as Fourier compositions

\[
\varepsilon_A(t) = \sum_{\omega} \varepsilon_{A\omega}\exp(-i\omega t), \tag{8}
\]

where the complex Fourier coefficients \(\varepsilon_{A\omega}\) and frequencies \(\omega\) must satisfy \(\varepsilon_{A(-\omega)} = \varepsilon_{A\omega}^*\) for \(\varepsilon_A(t)\) to be real-valued.

If \(\hat{H}\) is time dependent, eqn (5) does not conserve energy, \(E(\psi) = \langle \hat{\psi} | \hat{H} | \hat{\psi} \rangle\). However, if \(\hat{H}\) is time-periodic, a constant of motion can be derived by variation of the quasienergy, defined as the following time-averaged expectation value

\[
Q(\psi) = \left\langle \left\langle \langle \psi | \hat{H} | \psi \rangle - i \frac{\partial \langle \psi | \hat{H} | \psi \rangle}{\partial t} \right\rangle_T \right\rangle,
\]

where \(\psi\) must be normalized and periodic (same period as \(\hat{H}\)). Here, the outermost brackets denote time-averaging over one full period

\[
\langle \cdots \rangle_T = \frac{1}{T} \int_{t_0}^{t_0+T} (\cdots)dt, \tag{10}
\]

in which \(t_0\) is arbitrary since the quantity being time-averaged is periodic.

The variational condition is obtained by differentiating \(Q(\psi) = \langle \hat{\psi} | (\hat{H} - i \frac{\partial}{\partial t} - \lambda) | \psi \rangle_T\) with respect to \(\psi\), in which the (periodic) Lagrange multiplier \(\lambda(t)\) accounts for normalization, and then equating this derivative to zero

\[
2 \left( \hat{H} - i \frac{\partial}{\partial t} - \lambda \right) \psi = 0. \tag{11}
\]

Here, \(\lambda\) must be real-valued, as can be seen by applying \(\langle \psi |\), taking the imaginary part, and using that \(\psi\) is normalized. Furthermore, eqn (11) can be simplified by splitting \(\lambda\) into its average and oscillatory parts \(\lambda = Q + \partial f(\hat{t})/\partial t\), where \(Q = \langle \lambda \rangle_T\) and \(f(t)\) is periodic, followed by substituting \(\psi = \exp(i f)\psi\). After cancelling a net factor \(2\exp(f)\) and rearranging, we arrive at the simpler Floquet–Schrödinger eigenvalue equation

\[
\left( \hat{H} - i \frac{\partial}{\partial t} \right) \psi = Q \psi, \tag{12}
\]

where it becomes apparent why we use the same symbol for the average multiplier (eigenvalue), as for the integral in eqn (9). The corresponding solution of the time-dependent Schrödinger equation, eqn (5), is given by \(\psi = \exp(-iQt)\psi\). The existence of solutions of this form is known as Floquet’s theorem. We note that eqn (12) reduces to the time-independent Schrödinger equation if \(\hat{H}\) is time-independent (\(\hat{V} = 0, T\) arbitrary), and thus the quasienergy reduces to the energy, as expected.

In the following we will assume that all frequencies \(\omega\) in all perturbation strengths appearing in \(\hat{V}\) are multiples of a common fundamental frequency \(\omega_{o_0}\), i.e. \(\omega / \omega_{o_0} \in \mathbb{Z}\), and that \(\hat{H}\) therefore is periodic with period \(T = 2\pi / \omega_{o_0}\).
Since $\psi$ is variational it satisfies the (time-averaged) Hellmann–Feynman theorem, stating that $dQ/d\varepsilon_{\alpha\alpha}$ equals the time-averaged expectation value of the perturbing operator $\partial^2\psi/\partial\varepsilon_{\alpha\alpha}$, which turns out to be the frequency-$\omega$ Fourier coefficient of the first-order property (eqn (16))

$$\frac{dQ}{d\varepsilon_{\alpha\alpha}} = \left\{ \left\langle \psi \left( \frac{\partial^2\psi}{\partial\varepsilon_{\alpha\alpha}} \right) \right\rangle \right\}_T = \{ \exp(-i\omega t)\langle A(i) \rangle \}_T = \langle A(\omega) \rangle_{\alpha\alpha}.$$  

(13)

Although $\langle A(\omega) \rangle_{\alpha\alpha}$ is zero for $\omega \neq 0$ for our (time-independent) unperturbed wavefunction, second and higher-order derivatives, or molecular response functions, may be nonzero provided the sum of the frequencies is zero, e.g.

$$\langle A; B \rangle_{\alpha\alpha} = d(A)_{\alpha\alpha} = d^2Q_{\alpha\alpha} = \alpha$$

and the first frequency is therefore assumed to be minus the sum of the others, and conveniently omitted in the notation.

We notice from eqn (9) that time differentiation acts on $|\psi\rangle$, but not on its conjugate $\langle \psi|$. This asymmetry makes it difficult to reformulate the quasienergy $Q(\psi)$ in eqn (9) in terms of the (all-particle/unreduced) density operator $\hat{D} = |\psi\rangle\langle \psi|$, or reduced density matrices derived from $\hat{D}$, because these are inherently symmetric in $|\psi\rangle$ and $\langle \psi|$.

Fortunately, however, both the Floquet-Schrödinger eigenvalue equation, eqn (12), and the quasienergy derivative, eqn (13), are easily reformulated in terms of $\hat{D}$

$$\hat{H}\hat{D} - \hat{D}\hat{H} - i\frac{\partial \hat{D}}{\partial t} = 0, \ (\hat{D}\hat{D} = \hat{D}, \ Tr\hat{D} = 1)$$

(16)

$$\frac{dQ}{d\varepsilon_{\alpha\alpha}} = \left\{ \left\langle \psi \left( \frac{\partial^2\psi}{\partial\varepsilon_{\alpha\alpha}} \right) \right\rangle \right\}_T = \{ \exp(-i\omega t)\langle A(i) \rangle \}_T.$$  

(17)

We note the absence of the quasienergy eigenvalue $Q$ in eqn (16), known as the von Neumann equation (where we in parenthesis have noted that apply to $\hat{D}$, in addition to periodicity.) Thus, although we cannot easily determine the quasienergy of a solution $\hat{D}$ of eqn (16), we can, rather surprisingly, determine quasienergy derivatives to all orders.

Since any molecular property represents first- or higher-order corrections to the quasienergy, the quasienergy derivative defined for (in general) non-vanishing perturbation strengths contains all the necessary information needed for determining molecular properties.

At the SCF level of theory (for the electrons, with clamped nuclei), and employing generally time- and perturbation-dependent AO basis functions, eqn (16) becomes

$$FDS - i\frac{1}{2}S \left( \frac{\partial S}{\partial t} \right) - SDF - i\frac{1}{2} \left( \frac{\partial S}{\partial t} \right) S = 0,$$  

(18)

$$DSD = D, \ (\text{Tr} SD = N_{el})$$  

(19)

where $S$ is the overlap matrix, $D$ is the density matrix in the AO basis, which must satisfy the idempotency (and electron count) constraint given in eqn (19). The generalized AO Fock matrix $F$ is the (transposed) partial derivative of the following generalized energy

$$E(D) = \text{Tr} \left( h + V - \frac{i}{2} T \right) D$$

$$+ \frac{1}{2} \text{Tr} G^\dagger(D)D + E_{e\text{c}}[n(D)] + h_{\text{nuc}} + v_{\text{nuc}}$$

(20)

$$= E_{KS}(D) + \text{Tr} \left( V - \frac{i}{2} T \right) D + v_{\text{nuc}},$$

(21)

which in addition to the KS-DFT energy contains the interaction between perturbations and electrons $\text{Tr}VD$, and between perturbations and nuclei $v_{\text{nuc}}$ as well as an additional one-electron integral matrix arising from the time dependence of the basis functions, the antisymmetric time-differentiation integral matrix $T$

$$T_{x\lambda} = \langle x_{\lambda} | \frac{\partial \psi}{\partial t} \rangle - \langle x_{\lambda} | \frac{\partial \psi}{\partial t} \rangle, \ (22)$$

$$V_{x\lambda} = \langle x_{\lambda} | \hat{V}^\dagger \delta_{x_{\lambda}} \rangle = \sum_{A} \sum_{e} e_{Ae} \exp(-i\omega t) \langle x_{\lambda} | \hat{A}_{e} \rangle \delta_{x_{\lambda}} \delta_{x_{\lambda}}, \ (23)$$

$$v_{\text{nuc}} = v_{\text{nuc}} = \sum_{A} \sum_{e} e_{Ae} \exp(-i\omega t) \hat{A}_{nuc} \delta_{x_{\lambda}} \delta_{x_{\lambda}}, \ (24)$$

The remaining quantities introduced in eqn (18) and (20) are the overlap integrals $S$, one-electron integrals $h$, the two-electron integral matrix with $\gamma$-scaled exchange $G^\gamma$, and the nuclear repulsion energy $h_{\text{nuc}}$

$$S_{\lambda\lambda} = \langle \lambda_{\lambda} | \delta_{\lambda_{\lambda}} \rangle, \ (25)$$

$$h_{\lambda\lambda} = \langle \lambda_{\lambda} | -\frac{1}{2} \nabla^2 - \sum_{K} \frac{Z_{K}}{|R_{K} - R|} \delta_{\lambda_{\lambda}} \rangle, \ (26)$$

$$G_{\lambda\mu}^\gamma(M) = \sum_{\mu\nu} M_{\gamma\mu}(g_{\lambda\mu\nu} - \gamma g_{e\text{c}p\lambda\mu}), \ (27)$$

$$g_{\lambda\mu\nu} = \iint \lambda_{\lambda}(x_{\lambda}) \lambda_{\lambda}(x_{\lambda}) \frac{1}{r_{12}} \lambda_{\lambda}(x_{\lambda}) \lambda_{\lambda}(x_{\lambda}) dx_{\lambda} dx_{\lambda}, \ (28)$$

$$h_{\text{nuc}} = \sum_{A} \frac{Z_{A}}{|R_{A} - R|}, \ (29)$$

as well as the XC density functional $E_{e\text{c}}[n(D)]$, where $n$ is the electron density, which we will discuss in detail in section 3.4. We note that the HF energy is obtained as the special case $\gamma = 1, \ E_{e\text{c}} = 0$.}
For the quasienergy derivative, eqn (17), the corresponding formula within the SCF approximation is \(^{159}\)

\[
\frac{dQ}{de_{\alpha \beta}} = \left\{ \frac{\partial E(D)}{\partial e_{\alpha \beta}} - Tr \left( \frac{\partial S}{\partial e_{\alpha \beta}} \right) \right\}_T,
\]

(30)

\[W = DFD + \frac{i}{2} \left( \frac{\partial D}{\partial t} \right) SD - \frac{i}{2} DS \left( \frac{\partial D}{\partial t} \right),\]  

(31)

where the generalized energy-weighted density matrix \(W\) was introduced.

It is worth noting that the structure of the quasienergy derivative eqn (30) is very similar to that of the molecular gradient of Pulay\(^{23}\) as defined in eqn (1), the only difference being the modified expressions for the energy and energy-weighted density matrix.

The quasienergy derivative eqn (30) serves as a useful starting point for deriving (frequency-dependent) response functions, including the corrections due to perturbation dependence in the basis set, using the tools of (time-independent) energy-derivative theory.

We now introduce the following abbreviated notation for total derivatives of \(Q, D, F\), and \(W\), and partial derivatives of \(E(D)\) and integral matrices \(S\), etc., divided by the corresponding exponential phase factors

\[Q_{ab} = \frac{d}{de_{\alpha \beta}} Q, \quad D_{bc} = \frac{1}{\exp(-i(\omega_b + \omega_c)t)} \frac{d^2 D}{de_{\alpha \beta} de_{\gamma \delta}}, \]

(32)

\[E^{0,ab} = \frac{1}{\exp(-i(\omega_a + \omega_b)t)} \frac{\partial^2 E(D)}{\partial e_{\alpha \beta} \partial e_{\gamma \delta}}, \]

(33)

\[E^{2,ab} = \frac{1}{\exp(-i\omega_a \omega_b t)} \frac{\partial^3 E(D)}{(\partial D')^2 \partial e_{\alpha \beta}}, \]

(34)

where the \(\omega_a, \omega_b, \text{etc.}\) are the associated frequencies. When derivatives are taken at zero perturbation strength, the effect of the division is to remove the time-dependence of the derivative, which renders time-averaging \(\{ \ldots \}_T\) of the resulting formula redundant. Moreover, time-differentiation, as seen in eqn (18) and (31), applies before division by the phase factor, and results in an imaginary constant

\[
\frac{1}{\exp(-i(\omega_b + \omega_c)t)} \frac{d^3(D/\partial t)}{de_{\alpha \beta} de_{\gamma \delta}} = \frac{-i(\omega_b + \omega_c)}{\exp(-i(\omega_b + \omega_c)t)} D_{bc}.
\]

(36)

In this notation, compact expressions for linear- and quadratic response functions are obtained straightforwardly by differentiating eqn (30) with respect to additional perturbation strengths \(e_{\alpha \beta}\) and \(e_{\gamma \delta}\), and using the chain rule when differentiating \(E(D)\)

\[
Q_{ab} = E^{0,ab} + Tr E^{1,ab} D_b + Tr S_{ab} W + Tr S_{ab} W_b, \quad (37)
\]

\[
Q_{abc} = E^{0,abc} + Tr E^{1,abc} D_c + Tr E^{1,ab} D_c
+ Tr E^{2,ab} (D_b) D_c + Tr E^{1,ab} D_c - Tr S_{ab} W - Tr S_{ab} W_c + Tr S_{a} W_b + Tr S_{a} W_{ab}, \quad (38)
\]

The expressions in eqn (30), (37) and (38) follow the so-called \(n+1\) rule, meaning that perturbed parameters (here: density matrices) up to order \(n\) (0, 1 and 2, respectively), are used to compute a property of order \(n+1\) (1, 2 and 3, respectively). We note that for higher-order response functions, in many cases more efficient alternative formulas exist, which follow the \(2n+1, 2n+2\) etc., rules.\(^{159,166}\)

Expressions for the perturbed energy-weighted density matrices appearing in eqn (37) and (38) can be obtained by differentiating eqn (31), e.g.

\[
W^b = DF^b D + D^b \left( F + \frac{\partial F}{\partial S} \right) D + D \left( F - \frac{\partial F}{\partial S} \right) D^b, \quad (39)
\]

\[
W^{bc} = DF^{bc} D
+ D^{bc} \left( F + \frac{\partial F}{\partial S} \right) D + D^{bc} \left( F + \frac{\partial F}{\partial S} \right) D^b
+ D^{bc} \left( \frac{\partial F}{\partial S} \right) D + D^{bc} \left( \frac{\partial F}{\partial S} \right) D^b
+ D \left( F + \frac{\partial F}{\partial S} \right)^2 D + D \left( F + \frac{\partial F}{\partial S} \right)^2 D^b, \quad (40)
\]

where we have used eqn (36). Expressions for perturbed Fock matrices are obtained by differentiating eqn (21), and using the chain rule, e.g.

\[
F^b = E^{1,b} + E^2 (D^b), \quad (41)
\]

\[
F^{bc} = E^{1,bc} + E^2 (D^c) + E^2 (D^b) + E^3 (D^b, D^c) + E^2 (D^{bc}), \quad (42)
\]

Before we can compute response functions according to eqn (37) and (38), it remains to derive and solve equations for perturbed density matrices of different orders, \(D_b^b, D^b_c, D^{bc}, \text{etc.}\), which appear in these formulas. The first equation is derived by differentiating the idempotency constraint, eqn (19), and collecting terms involving the solution (highest-order density matrix) on the left-hand side.\(^{159,167}\)

\[
D^b S_D + D^b D^b - D^b = - D^b S_D, \quad (43)
\]

\[
D^{bc} S_D + D^{bc} D^{bc} - D^{bc} = - (D^{bc} S_D + D^b S^c D)
+ D^b S^b D + D^{bc} S^c D + D^{bc} S^c D + D^b S^c D + D^{bc} S^c D, \quad (44)
\]

Both these and corresponding higher-order equations are of the general form

\[
D^b \quad S_D + D^b S_D \cdot D^b \cdot D^b \cdot D^b = N, \quad (45)
\]

where right-hand sides \(N\) contain perturbed overlap matrices and already determined lower-order density matrices. The general solution is of the form\(^{159}\)

\[
D^b = D^b + D^b D^b, \quad (46)
\]

\[
D^b = NSD + DSN - N, \quad (47)
\]

\[
D^b = XSD - DSB, \quad (48)
\]
where the solution \( D^h \) is partitioned into a particular component \( D^h_{\text{part}} \), which solves eqn (45), and a homogeneous component \( D^h_{\text{hom}} \), parameterized by an unknown matrix \( X \), which solves the corresponding homogeneous equation (eqn (45) with \( N = 0 \), as can be seen by inserting in eqn (45) and using eqn (19). We note that in a basis of occupied and virtual molecular orbitals, the particular component \( D^h_{\text{part}} \) has nonzero elements only in the occupied–occupied and virtual–virtual blocks, whereas the homogeneous component \( D^h_{\text{hom}} \) has nonzeros only in the occupied–virtual and virtual–occupied blocks.

It remains to determine the homogeneous component \( D^h_{\text{hom}} \). Differentiating eqn (18), and collecting terms involving the yet undetermined homogeneous components on the left-hand side

\[
E^2(D_h^h)DS - SD E^2(D_h^h) + FD_h^h S - SD_h^h F - \omega_h SD_h^h S
\]

\[
= - \left[ E^{1,h} + E^{2,h}(D_h^h) \right] DS - \left( F - \frac{\omega_h}{2} S \right) \left( D_h^h S + DS_h^h \right) + \left[ S^h D + SD_h^h \right] \left( F + \frac{\omega_h}{2} S \right)
\]

\[
E^2(D_h^h)DS + FD_h^h S - SD E^2(D_h^h) - SD_h^h F - (\omega_h + \omega_t) SD_h^h S
\]

\[
= \left[ E^{1,h} + E^{2,h}(D_h^h) \right] DS + \left[ S^h D + SD_h^h \right] \left( F + \frac{\omega_h}{2} S \right) + \left( F - \frac{\omega_h}{2} S \right) \left( D_h^h S + DS_h^h \right) + \left( S^h D + SD_h^h \right) \left( F + \frac{\omega_h}{2} S \right)
\]

In deriving these equations, we have used the chain rule to expand the highest-order Fock matrices \( F^{h-c} \), as well as eqn (36) to expand time-derivatives. As was the case with the idempotency constraint, eqn (43) and (44), the equations are of the same general form

\[
E^2(D_h^h)DS + FD_h^h S - SD E^2(D_h^h) - SD_h^h F - (\omega_h + \omega_t) SD_h^h S = M
\]

where right-hand sides \( M \) contain perturbed integral matrices and already determined lower-order density and Fock matrices. Therefore, parameters \( X \), which define homogeneous components \( D^h_{\text{hom}} \), can be determined to any order by solving linear response equations of the form

\[
(E^{[2]} - \omega S)^2 X = M
\]

where the electronic Hessian \( E^{[2]} \) and metric operator \( S^{[2]} \) in the AO basis are defined as \(^{158,167,168}\)

\[
E^{[2]} = E^{2}(XSD - DSX)DS + F(XSD - DSX)S - SD E^{2}(XSD - DSX) - S(XSD - DSX)F
\]

\[
S^{[2]} = S(XSD - DSX)S
\]

It is worth noting that the form of eqn (52) is independent of the order of the perturbed density matrix, the only difference being the form of the right-hand side in eqn (52). We have thus obtained a recursive procedure for generating higher-order perturbed density matrices from the lower-order ones, as already exploited in the case of one-electron perturbing operators,\(^ {62,63,79}\) but our eqn (52) is applicable also for perturbation-dependent basis sets.

The generic form of the linear response equation in eqn (52) is the same as the linear response equations that appear in conventional response theory formulated in the molecular-orbital (MO) basis,\(^ {54,169}\) in two- and four-component relativistic response theory,\(^ {169}\) as well as in the case of AO-based linear scaling response formulations.\(^ {158,168}\) All the complexity of the Hamiltonian and the representation of the SCF wave function is hidden in the solution of the response equation eqn (52) and in the approach for determining the SCF energy, whereas the equations that determine the quasiequilibrium derivatives remain the same.

The work presented in ref. 159 and summarized here therefore provides a general, open-ended quasiequilibrium response theory framework for which the working equations of the quasiequilibrium derivatives are independent of the wave function parameterization and the exact form of the Hamiltonian, allowing for a broad range of applications of the formalism. However, in order for the formalism to be utilized in actual computations, several building blocks need to be present. In particular, we need to have: (1) A program for optimizing SCF states in the relativistic or nonrelativistic domains, as well as a program to solve frequency-dependent HF/KS response equations, eqn (52), to determine perturbed density matrices; (2) A general one-electron integral program capable of handling the many different operators that arise when differentiating the different one-electron integrals that appear in our interaction Hamiltonian \( F^e \) with respect to nuclear displacements or external magnetic fields; (3) A code for calculating arbitrary-order derivatives of the two-electron repulsion integrals; (4) An arbitrary-order derivative code for calculating XC functional derivatives and XC potential and kernel matrix elements, which should also include the effects of geometric and magnetic perturbations. In the following, we will briefly describe our efforts in developing these different building blocks, and in this way generate a complete toolbox for the calculation of any molecular property, the only limitation being that the molecule has to be described by an SCF state, and that perturbation theory still remains valid for describing the interactions of the perturbations with the molecule.

### 3.2 Extension to the relativistic domain

Without specifying the actual Hamiltonian, all the above equations hold both in nonrelativistic and relativistic frameworks, whether the wave function is constructed from...
one-component orbitals or from two- or four-component spinors. The general framework for the calculation of arbitrary-order molecular properties which is outlined in this paper is a method and can be used and developed relatively independently of the Hamiltonian as far as the general equations of the density-matrix-based response theory are concerned. However, when considering the actual solution of the response equations, the calculation of molecular properties in the relativistic domain is different in some aspects: A feature that fundamentally distinguishes four-component relativistic response calculations from two- and one-component implementations is the fact that negative-energy solutions of a four-component relativistic Hamiltonian appear as additional degrees of freedom when determining the time-dependent self-consistent-field equations. Another fundamental difference is the loss of spin symmetry in calculations including the spin–orbit coupling. We will return to both of these features. The advantage of maintaining a very generic formulation of the response theory, hiding the above-mentioned differences between non-relativistic and relativistic theory at a different implementational level, is that we may arrive at a versatile implementation of the response theory in which the user can calculate in principle any molecular property for an arbitrary self-consistent-field reference state and choose from a menu of one-, two-, and four-component Hamiltonians.

Our presently available menu of Hamiltonians consists of, in addition to the standard non-relativistic one-component Hamilton, the four-component relativistic Dirac–Coulomb (DC) Hamiltonian, the computationally advantageous one-step, exact two-component (X2C) Hamiltonian, the spin-free modified Hamiltonian where the spin–orbit coupling is selectively eliminated, and the four-component nonrelativistic Levy–Leblond Hamiltonian, where both scalar relativistic effects and spin–orbit coupling are eliminated.

The four-component relativistic Hamiltonian in the Born–Oppenheimer approximation and in the absence of external fields other than the scalar potential created by the nuclei, may be written as a sum of one- and two-electron terms plus the classical nuclear electrostatic repulsion:

\[ H = \sum_i [\hat{h}_{\text{DC}}(i) + \hat{V}^\text{ne}(i)] + \frac{1}{2} \sum_{i\neq j} \hat{g}(i,j) + V^\text{nn}. \]  

(55)

Here, \( \hat{V}^\text{ne}(i) \) describes the interaction of electron \( i \) with the scalar potential created by the nuclei, and the free-particle Dirac operator \( \hat{h}_{\text{DC}} \) is given by

\[ \hat{h}_{\text{DC}} = \begin{bmatrix} 0_{2 \times 2} & c(\sigma \cdot \mathbf{p}) \\ c(\mathbf{p} \cdot \sigma) & -2c^2 \mathbf{1}_{2 \times 2} \end{bmatrix}, \]  

(56)

where \( c \) is the speed of light, and \( \sigma \) is the vector of Pauli spin matrices in the standard representation. A closed-form expression for the Lorentz-invariant two-electron interaction is not available and \( \hat{g}(i,j) \) is approximated in the DC Hamiltonian to zeroth order by the instantaneous Coulomb interaction

\[ \hat{g}^c(i,j) = (1_{4 \times 4} \otimes 1_{4 \times 4})r^{-1}. \]  

(57)

This operator provides the spin-same, but not the spin-other orbit interaction. In this Hamiltonian, the Gaunt interaction and all higher-order corrections are neglected. The other Hamiltonians mentioned above are discussed in more detail in the context of response theory for instance in ref. 169 and we shall not repeat the discussion here.

In the two- and four-component relativistic HF and KS methods employed in our program, bound electronic states are described by a Slater determinant of orthonormal (in general complex) two- and four-component one-electron spinors. For a discussion of the self-consistent-field optimization of the four-component relativistic closed-shell wave function, see for instance ref. 181. In addition to a scheme for optimizing self-consistent-field states, the extension of the density-matrix-based response theory to the relativistic domain requires interfaces to a relativistic linear response solver and to relativistic integrals. These building blocks are to a large extent provided by the DIRAC program, whereas more specialized integrals are provided by GEN1NT. Two-, and in particular four-component, relativistic methods come with an increased computational cost compared to one-component (non-relativistic) methods due to the possibly large basis set that needs to be used as well as the larger number of wave function parameters. However, recent developments have demonstrated that these challenges can largely be overcome, making relativistic calculations comparable in cost to non-relativistic calculations.

We can now return to the features which make the solution of the time-dependent self-consistent-field equations different from nonrelativistic calculations, and we will first consider the appearance of the negative energy solutions as additional degrees of freedom. Using an exponential parametrization of the perturbed determinant

\[ |\psi(\mathbf{k})\rangle = \exp[-\mathbf{k}|(|\psi\rangle \right) \]  

(58)

where we have introduced the second quantization excitation \( \hat{a}^\dagger \) and de-excitation operators \( \hat{a}_i \), and solving for the non-redundant first-order orbital rotation amplitudes \( \kappa_{\alpha\beta} \) between virtual (index \( a \)) and occupied (index \( \alpha \)) MOs, the additional degrees of freedom are rotations between virtual negative-energy and occupied positive-energy orbitals. In the case of applied electric perturbations, these additional degrees of freedom give only very minor corrections to the calculated properties, in general five to six orders of magnitude smaller contributions. However, these contributions may be significant, and in many cases dominating, when magnetic perturbations are considered. In the case of magnetic perturbations, these additional contributions also have a physical interpretation. Pyykkö, Aucar et al., and Kutzelnigg have demonstrated that this contribution to the response functions corresponds to diamagnetic terms in nonrelativistic theory. In the four-component relativistic framework, both paramagnetic and diamagnetic terms are obtained from a single operator. This simplification of the magnetic operators in the four-component relativistic framework makes the implementation of magnetic properties easier since both paramagnetic and diamagnetic terms are calculated at the same time using a
uniform theoretical framework. We note that relativistic effects on NMR properties in many cases can be very large.28,29

A second difference in relativistic compared to nonrelativistic theory, is that in the latter case, the spin and spatial degrees of freedom are completely decoupled, and spin—and in the case of atoms also the orbital angular momenta—have good quantum numbers. When spin–orbit coupling is introduced through the Dirac equation, this nonrelativistic symmetry is lost. To some extent, time reversal symmetry can recover the spin symmetry lost in the relativistic framework and in our implementation we fully exploit the symmetry scheme proposed by Saue and Jensen169 based on quaternion algebra, which automatically provides the maximum point group and time reversal symmetry reduction of the computational effort for the point group D2h and subgroups.

3.3 Molecular integrals

For the implementation of an open-ended response scheme, we need to be able to calculate molecular one- and two-electron integrals to arbitrary order in the perturbations. Let \( \chi_\alpha(r) \) be an AO as given in eqn (3). The necessary integrals are of the form

\[
O_{\alpha\beta} = \int \chi_\alpha^*(r) \hat{O} \chi_\beta(r) \, dr,
\]

where, in the multi-index notation \( A^a = A^a_x \hat{A}^a_y \hat{A}^a_z \) and \( \partial^a = (\partial/\partial A_x \hat{A}^a_y \hat{A}^a_z)^{\hat{A}^a_y \hat{A}^a_z} \), the operator \( \hat{O} \) takes the general form

\[
\hat{O} = f(r_c) R^k_{\alpha\beta} r_{\beta\alpha}^m \delta^m_{\alpha\beta},
\]

consisting of four factors. The factor \( f(r_c) \) is a function of the distance \( r_c \) of the electron from \( C \)—for example, the position of a nucleus or a charge defining a molecular-mechanics system in a quantum-mechanics/molecular-mechanics (QM/MM) calculation. Here, we restrict ourselves to the form \( f(r_c) = r_c^{-m_0} \) with \( m_0 = 1.2 \) but note that other forms such as the Dirac delta function and \( m_0 = 0 \) have also been implemented.32 The second factor \( R^k_{\alpha\beta} \) in eqn (61) depends on the relative position \( R_{c\beta} = R_c - R_\beta \) of AOs in \( O_{\alpha\beta} \), whereas the third factor \( r_{\beta\alpha}^m \) depends on the position of the electron relative to a center \( M \) such as the origin of a multipole expansion. Finally, the fourth factor \( \delta^m_{\alpha\beta} \) in eqn (61) is a general differential operator. The operator \( \hat{O} \) thus covers a large variety of interactions and perturbations as needed for an open-ended response approach. In addition, perturbation dependence is introduced into the one- and two-electron integrals through the perturbation dependence of the AOs, see eqn (3).

The solid-harmonic Gaussian functions \( S_{\nu,m_\alpha}(r_x) \) in eqn (3) are not separable in the Cartesian directions. Much of the evaluation of molecular integrals is therefore carried out over a set of auxiliary separable Gaussians, from which the final integrals are assembled. There are two useful separable Gaussians: the Cartesian and Hermite Gaussians, defined as

\[
G^k_{\alpha}(r_x) = r_x^k \exp(-ar_x^2),
\]

\[
H^k_{\alpha}(r_x) = (2a)^{-|k|} \partial^k_{r_x} \exp(-ar_x^2),
\]

from which the primitive solid-harmonic Gaussian functions are obtained as

\[
S_{\nu,m_\alpha}(r_x) \exp(-ar_x^2) = \sum_{|k|=\nu} S^k_{\nu,m_\alpha} G^k_{\alpha}(r_x) = \sum_{|k|=\nu} S^k_{\nu,m_\alpha} H^k_{\alpha}(r_x).
\]

Remarkably, the solid-harmonic expansion coefficients \( S^k_{\nu,m_\alpha} \) are the same in the two cases.189 The traditional choice of separable Gaussians are the Cartesian ones. However, an advantage of the Hermite Gaussians is that differentiation with respect to nuclear positions merely raises the quantum numbers

\[
\partial^{|n|}_{R_x} S_{\nu,m_\alpha}(r_x) \exp(-ar_x^2) = (2a)^{|n|} \sum_{|k|=\nu} S^k_{\nu,m_\alpha} H^{|n|+k}_{\alpha}(r_x),
\]

simplifying the development of an open-ended code with respect to geometric differentiation.

Let us first consider the evaluation of the one-electron integrals of eqn (59). Restricting ourselves to AOs without London phase factors, we obtain\(^3\)

\[
\partial^{|n|}_{R_x} S_{\nu,m_\alpha}(r_x) = (2a)^{|n|} \sum_{|k|=\nu} S^k_{\nu,m_\alpha} H^{|n|+k}_{\alpha}(r_x),
\]

as a linear combination of integrals over Hermite Gaussians, whose recurrence relations depend on \( f(r_c) \); in ref. 52, such relations are given for \( f(r_c) = r_c^{-1}, r_c^{-2}, \delta(r_c), \) and 1. Based on these recurrence relations, we have developed a tool package GEN1NT,\(^3\) where we have provided an interface using the Q5Cost library.\(^90,92\) The package was further implemented into a development version of DALTON.\(^93\) Providing all integrals that may become necessary for geometric and magnetic derivatives of the many possible interaction Hamiltonians of interest, GEN1NT is an essential element in the development of an open-ended approach for molecular properties with PDBSs. We have recently extended it to consider the challenges faced when introducing LAOs as well as allowing effective core potentials and model core potentials to be used in the calculations.\(^53\)

Turning our attention to the two-electron integrals over London AOs in eqn (60), we first note that these are independent of the gauge origin \( G \), which cancels out in the overlap distributions \( \chi_{\nu\lambda}^x \chi_{\lambda}^\lambda \) and \( \chi_{\nu\lambda}^x \chi_{\lambda}^\nu \):

\[
\chi_{\nu\lambda}^x = \exp\left(\frac{i}{2} \sum_{\beta} B \cdot R^x_{\nu\lambda} \times r_\beta \right) \chi_{\nu}(r_\nu) \chi_{\lambda}(r_\lambda) \theta_x(r_\nu) \theta_x(r_\lambda),
\]

but do depend on the phase-factor origin \( P \). Differentiation with respect to the magnetic field \( B \) multiplies \( \chi_{\nu\lambda}^x \) by the corresponding element of the vector

\[
\frac{1}{2} \sum_{\nu} R^x_{\nu\lambda} \times r_\nu \partial^{|n|}_{R_\nu} \chi_{\nu\lambda}^x |_{\lambda=0} = \left( \frac{|n|}{7} \right) \left( R^x_{\nu\lambda} \times r_\nu \right)^{|n|} \chi_{\nu\lambda}^x.
\]
which we obtain by contracting the elements of the simpler distributions \( r_p^* \gamma_{\mu} \). Since this contraction depends on \( R_a \) and \( R_b \), derivatives with respect to these centers contain lower-order derivatives such as

\[
\frac{\partial^2 \gamma_{\mu} \gamma_{\nu}}{\partial X_{ik} \partial B_j} \bigg|_{B=0} = \frac{i}{2} (2 \alpha_{ik} x_p - X_{ik} z_p) \frac{\partial r_p^*}{\partial X_{ik}} \gamma_{\nu} - \frac{i}{2} z_p^* \gamma_{\nu} \gamma_{\mu} .
\]

(69)

Given that \( R_{a,k} \times r_p \) has only two linearly independent components, \( (R_{a,k} \times r_p)^m \) has \( m+1 \) rather than \( (m+1)(m+2)/2 \) independent components of \( m \).

The product of two Gaussians is a scaled Gaussian centered somewhere on the line between the two centers, a property known as the Gaussian product rule.394

\[
\exp(-u_{ij} \gamma_{k}^2) \exp(-u_{ij} R_{a,k}^2) = \exp(-u_{ij} R_{a,k}^2) \exp(-u_{ij} R_{b,k}^2),
\]

(70)

where we have introduced the following quantities

\[
p_{ij} = a_{ij} + b_{ij}, \quad u_{ij} = a_{ij} b_{ij}, \quad R_a = a_{ij} R_b + b_{ij} R_c. \quad (71)
\]

Differentiation with respect to \( R_{a,k} \) and \( R_{b,k} \) results in polynomial factors multiplying \( \exp(-p_{ij} R_{a,k}^2) \). Thus, starting from the integrals over \( H_{a,b}^k(R_{a,b}), s \leq k + 1 + m \), which are Hermite polynomials multiplied by \( \exp(-p_{ij} R_{a,k}^2) \), integrals over the target distributions \( r_p^* H_{a,b}^k(R_{a,b}) H_{b,c}^l(R_{b,c}) \) are obtained by polynomial translation (or momentum transfer). We have implemented this approach by recursion over the auxiliary distributions

\[
\{smkl\} = \left( \frac{\partial R_a + \partial R_b + \partial P}{2 p_{ij}} \right)^s \left( \frac{\partial R_a + \partial R_b + \partial P}{2 b_{ij}} \right)^l \times \exp(-a_{ij} R_{a,k}^2) \exp(-b_{ij} R_{b,l}^2),
\]

(72)

among which the target distributions are found as \( \{0mkl\} \).

Two-electron integrals are invariant under a net translation of all centers of the integrand, generated by the operator

\[
\partial_{R_a} + \partial_{R_b} + \partial_{P} + \partial_{R_a} + \partial_{R_b} + \partial_{P} = 0, \quad (73)
\]

where \( R_a \) and \( R_b \) are the centers of the basis functions for the second electron, \( \gamma_{a,b}(R_a) \) and \( \gamma_{a,b}(R_b) \) in eqn (60). For the sake of derivation, we here distinguish the phase-factor origin for the second electron \( P \) from that of the first electron \( P \), although these are required to be identical. Rearranging, scaling and powering gives

\[
\left( \frac{\partial R_a + \partial R_b + \partial P}{2 p_{ij}} \right)^s \times \left( \frac{\partial R_a + \partial R_b + \partial P}{2 b_{ij}} \right)^l
\]

(74)

where \( q_{ij} = c_{ij} + d_{ij} \) the sum of exponents of \( \gamma_{a,b} \) and \( \gamma_{a,b} \) respectively. This equation states that excess momentum on \( s \) in eqn (72) for the first electron, can be transferred to the second electron by a simple scaling. Then, after contracting over exponents \( a_{ij} \) and \( b_{ij} \) and contracting the distributions for the first electron to the solid-harmonic basis, the recursion procedure can be repeated for the second electron, giving us the final expression for the two-electron integral.389

3.4 Higher-order exchange–correlation kernels

To calculate arbitrary-order molecular properties for a KS-DFT reference state, we must construct derivatives of the XC part of the KS potential, kernel, and higher-order kernel matrices with respect to perturbation field strengths, geometric displacements, and their London AO magnetic derivatives.

Although HF is quadratic in the one-particle density matrix, whereas KS-DFT is nonlinear (non-polynomial), as seen in eqn (20), they are similar from an implementational point of view. Specifically, to extend an open-ended HF response code to KS-DFT, we add the XC contribution and either scale (hybrid functionals: \( 0 < \gamma \leq 1 \)) or remove (non-hybrid functionals: \( \gamma = 0 \)) the (HF- or exact-) exchange contribution in eqn (27). The starting point for the former is the XC energy for a generalized-gradient-approximation (GGA) functional, which can be written as the integral over the XC energy density

\[
E_{xc} = \int \delta_{xc}(n,s) (\nabla n, \nabla s, \nabla s) dr,
\]

(75)

a function of five local variables that depend on the charge density

\[
n(r) = \sum_i \phi_i^*(r) \phi_i(r) = \sum_{\mu \nu} \Omega_{\mu \nu}(r) D_{\mu \nu},
\]

(76)

the spin density (non-collinear definition)

\[
s(r) = |s(r)| \quad \text{with} \quad s(r) = \sum_i \phi_i^*(r) s \phi_i(r),
\]

(77)

and their Cartesian gradients. Functionals on higher rungs of the Jacob’s ladder of XC approximations495 and other generalized KS-DFT theories contain additional variables such as the kinetic energy density, the Laplacian, current density, vorticity, and so on. For simplicity, we do not discuss these variables, considering only traditional GGA functionals.

Using the ansatz of eqn (75), we can express the XC potential matrix elements in the AO basis, \( K_{xc,kl} \), in the following compact and computationally advantageous form:

\[
K_{xc,kl} = \int \frac{\partial \Omega_{xc}}{\partial D_{kl}} dr = \left[ \int \{ \int \left( \sum_{i=x,y,z} u_{i} \Omega_{xc} + v_{0} \cdot \nabla \Omega_{xc} + \sum_{i=x,y,z} v_{i} \cdot \nabla \Omega_{xc} \right) dr \right] \right.
\]

(78)

The integrand contains the AO product, \( \Omega_{xc} \), its Cartesian gradient, \( \nabla \Omega_{xc} \), and their non-collinear spin density counterparts \( \Omega_{xc} \) and \( \nabla \Omega_{xc} \) with \( \Omega_{xc} = \gamma_{a,b} \sigma_{l} \gamma_{a,b} \) and \( \sigma_{l} \) being one of the Pauli spin matrices \( (l = x,y,z) \). In the collinear approximation, only the \( z \)-component of the spin density is considered and the \( x \)– \( y \)-terms are neglected. The integrand also contains scalar and vector prefactors \( u \) and \( v \),...
respectively, which, in the unperturbed case, contain first-order XC functional derivatives with respect to the density variables of eqn (75):

\[ u_0 = \frac{\partial \varepsilon_{xc}}{\partial n}, \]  
\[ u_i = \frac{s_i}{s} \frac{\partial \varepsilon_{xc}}{\partial s}, \]  
\[ v_0 = \nabla n \left( \frac{\partial \varepsilon_{xc}}{\partial (n \cdot \nabla s)} + 2 \frac{\partial \varepsilon_{xc}}{\partial (n \cdot \nabla n)} \right), \]  
\[ v_i = \nabla s_i \left( \frac{\partial \varepsilon_{xc}}{\partial (n \cdot \nabla s)} + 2 \frac{\partial \varepsilon_{xc}}{\partial (s_i \cdot \nabla s)} \right), \]

evaluated at the closed-shell reference state for which \( s = 0 \) and \( i = x, y, z \).

Due to the nonlinear form of the XC functionals, the integration of the XC potential matrix elements in eqn (78) is performed numerically, evaluating the integrand at typically \( 10^4 \) to \( 10^6 \) grid points for small to medium-sized molecules. The numerical integration grid is an additional parameter of KS-DFT response calculations, which must be well adapted to the property under study, much like the response of the density matrix must be accurately represented by the AO basis for the results to be meaningful.

In order to construct derivatives of the XC potential to obtain the XC kernel, and higher-order kernel matrices when calculating molecular properties, one can make use of the generic computational form of eqn (78) with modified scalar and vector prefactors \( u \) and \( v \) which contain—according to the chain rule—every order of perturbation a growing number of products of perturbed density variables and XC functional derivatives. A considerable technical challenge is that XC functional derivatives appearing in the perturbed prefactors \( u \) and \( v \) are needed to the same order as the order of the quasienergy derivative. Since most of the modern XC functionals involve rather complicated expressions, higher-order derivatives are often out of reach for manual differentiation.

The required derivatives can alternatively be generated using symbolic differentiation techniques (see e.g. ref. 196 and 197) but this approach still requires manual intervention and verification, and typically generates rather lengthy code (since every necessary derivative is implemented separately for each functional). Generating functional derivatives via automated symbolic manipulation is therefore not likely to be a viable approach for calculating higher-order XC contributions, although implementations of response functions based on this scheme have been presented in the literature. A solution to this problem has recently been presented by Ekström et al. using automatic differentiation (AD). The approach of Ekström et al. starts from a computer implementation of the XC energy functional, from which analytic arbitrary-order derivatives are generated automatically using an AD library based on operator overloading. We will briefly discuss the principles of AD before we proceed to consider how to determine the expressions for the higher-order XC kernels, in particular when also the corrections arising from the use of PDBS are considered.

### 3.4.1 Principles of automatic differentiation

Automatic differentiation is a well-established method in computer science, but its use in quantum chemistry has been very limited. The underlying principle of AD is that any computer program is a collection of very basic operations. The derivatives of these basic operations are known and often trivial. One can thus produce codes that will manipulate these basic operations and in this way for instance automatically differentiate a mathematical expression implemented in a computer program. The important point that distinguishes AD from symbolic differentiation, as exemplified by for instance using Mathematica to obtain analytic expressions for XC derivatives, is that the differentiated quantity is obtained from an existing implementation of an XC functional, not by generating explicit code for the derivative of the XC functional itself. In our implementation, the size and structure of the parent code is retained, with the difference that the basic operations on floating points numbers are replaced by operations on truncated Taylor polynomials.

Since AD is fairly new as a tool in quantum chemistry, we believe it is valuable to explore the principles of AD by an example, using the example already given in ref. 160, namely the simple Slater exchange functional given for pedagogical reasons as \( \varepsilon_e(n) = C(n^4) \), with \( C = -0.93 \) being a constant. Let us now assume that we want to calculate the second derivative of this functional at a reference density \( n_0 = 2.0a_0^{-3} \). By representing the building blocks of the functional in terms of their Taylor expansions, and acting on these Taylor expansions with the elementary mathematical operations, we will obtain a Taylor expansion expression for \( \varepsilon_e(n) \) at \( n_0 = 2.0a_0^{-3} \) that will also contain the derivatives to this predetermined order.

We note that if we are only concerned with the second derivatives of the Slater exchange functional, we only need a Taylor expansion of our density to second order in the density variations. We can therefore write our density as

\[ n = 2.0 + 1.0 \delta_N + 0.0 \delta_N^2, \]

with the 1.0 coefficient expressing the trivial fact that \( \partial n/\partial n = 1 \). In the computer program, only the Taylor expansion coefficients 2.0, 1.0, 0.0 are stored, and the approach is thus fully numerical.

From the non-standard way of writing \( \varepsilon_e \), we start by evaluating \( n^4 \) of the Taylor expansion in eqn (83)

\[ n^4 = (2.0 + 1.0\delta_N)^4 = 16.0 + 32.0\delta_N + 24.0\delta_N^2 + O(\delta_N^3), \]

where we can truncate the higher-order contributions, thus reducing the number of floating-point operations that are needed. We now need to consider the cube root of this expression. However, the cube root is by itself a non-trivial operation. The code will in this case expand the cube root function in a new Taylor series, truncated at second order, around the new expansion point 16.0, giving us

\[ (16.0 + \delta z)^{1/3} = 2.5 + 0.052\delta z - 0.0011\delta z^2 + O(\delta z^3). \]
Inserting $\delta z = n^4 - 16.0 = 0.0 + 32.0 \delta_N + 24.0 \delta_N^2$ into eqn (85), truncating at second order, we get

$$\left(n^4\right)^{1/3} = 2.5 + 1.7 \delta_N + 0.14 \delta_N^2 + O(\delta_N^3). \quad (86)$$

Finally, multiplying with the overall factor of $-0.93$ we get the Taylor expansion of the Slater exchange functional as

$$C(n^4)^{1/3} = -0.93 \times (16.0 + 32.0 \delta_N + 24.0 \delta_N^2)^{1/3} = -2.3 - 1.6 \delta_N - 0.13 \delta_N^2 + O(\delta_N^3) \quad (87)$$

The Taylor expansion of the Slater exchange functional in eqn (87) contains the zeroth-, first- and second-order derivatives of the functional, and we thus now know the functional value of the second derivative of the functional for $n = 2.0 a_0^{-3}$, namely $-0.13 a_0^{-9}$. We emphasize that this number is numerically exact save for round-off errors, and that no finite difference or analytic manipulations of the functional have been made. By comparing the results obtained in double and quadruple precision calculations, we have demonstrated that AD gives high-order derivatives that are correct to at least 12 significant digits in double precision, even for very small or very large values for the densities, and close to 16 significant digits for density values in a normal range.

Using the principles of automatic differentiation, we have written a general-purpose library for evaluating derivatives to arbitrary order of any given XC functional. There are two key elements in making such a library: (1) Developing a code that for all kinds of elementary mathematical functions $f(x)$ not only returns the value of the function itself, but also all its derivatives $f^{(i)}(x)$ to an arbitrary but predefined order $i$, and then representing these mathematical functions by their Taylor expansions; and (2) Replacing all elementary scalar mathematical operations by operations that act on these finite-order Taylor expansions and in particular their floating-point coefficients. This is achieved by using the principles of operator overloading. We do not discuss these details here, referring instead to the paper by Ekström et al.

### 3.4.2 Construction of higher-order XC kernel matrix elements

Having access to arbitrary-order XC functional derivatives and arbitrary-order density variables (evaluated using arbitrary-order perturbed density matrices) allows us to construct in principle arbitrary-order XC kernel matrix elements. For perturbations which do not modify the AO overlap (such as electric perturbations and magnetic perturbations using field-independent AOs and a common gauge origin) expressions for XC kernel matrix elements up to quartic response ignoring spin density contributions can be found in ref. 202. These expressions are very lengthy at higher orders but they can be obtained by straightforward (automatizable) application of the chain differentiation rule. Also the missing spin density terms can be added analogously to the spin density independent contributions (see e.g. ref. 203).

In this perspective article we will not repeat these lengthy expressions but rather discuss XC contributions arising from perturbations which modify the AO overlap such as geometric perturbations and magnetic perturbations using London AOs and for simplicity ignore spin density dependence. Geometric derivatives of KS potential/kernel matrices require the calculation of additional functional derivatives and additional AO Cartesian derivatives. Each order of geometric derivative (one for the molecular gradient, two for the Hessian, etc.) increases the highest functional derivative order by one and the highest AO Cartesian derivative by one, reflecting the chain differentiation rule. This means that the $M'$th-order geometric derivative of an $N$th-order property requires $(N + M')$th-order functional derivatives, $M'$th-order AO derivatives for local density approximation (LDA)-type functionals and $(M + 1)'$th-order derivatives for GGA functionals. In order to discuss London AO magnetic derivatives of XC matrix elements, it is useful to consider the terms $(u_0 \Omega_{kl})$ and $(\nabla n \Omega_{kl})$ of eqn (78) separately. As already pointed out in section 3.3, the effect of (repeated) B differentiation of the London AO product $\Omega_{kl}$ can be expressed as the standard AO product $\tilde{\Omega}_{kl}$ (repeatedly) multiplied with components of the vector

$$V_{rp} \equiv \frac{i}{2} (R_{kl} \times r_p). \quad (88)$$

The same is true for the terms $(u_0 \Omega_{kl})$ appearing in eqn (78):

$$\frac{\partial}{\partial B_i} \left( v_{0} \cdot \nabla \Omega_{kl} \right) = V_{rp} V_{jp} \frac{\partial}{\partial B_j} \left( u_0 \cdot \nabla \Omega_{kl} \right). \quad (89)$$

The $B$ differentiation of the London AO terms $(v_{0} \cdot \nabla \Omega_{kl})$ also corresponds to a multiplication with components of the vector $V_{rp}$, but additional terms containing the undifferentiated AO product also appear in this case. A first-order differentiation generates

$$\frac{\partial}{\partial B_i} \frac{\partial}{\partial B_j} (v_{0} \cdot \nabla \Omega_{kl}) = V_{rp} V_{jp} \frac{\partial}{\partial B_j} (u_0 \cdot \nabla \Omega_{kl}) + V_{rp} V_{jp} \frac{\partial}{\partial B_j} (v_{0} \cdot \nabla \Omega_{kl}) = V_{rp} V_{jp} \left( \frac{\partial}{\partial B_j} (u_0 \cdot \nabla \Omega_{kl}) + \frac{\partial}{\partial B_j} (v_{0} \cdot \nabla \Omega_{kl}) \right). \quad (90)$$

Higher-order contributions can be accessed accordingly. Turning now to geometric derivatives, the evaluation of XC contributions to geometric gradients of molecular properties is from the implementational point of view more involved than the evaluation of LAO XC terms. The reason for this is that the XC energy density variables $n$ and $(\nabla n \cdot \nabla n)$ explicitly depend on the position of the nuclei and their displacements, in contrast to the $B$ differentiation which leaves them unmodified. This generates additional terms by the chain differentiation rule. Returning to the XC potential matrix elements, eqn (78), which we now write in a more general form

$$K_{\text{xc}kl} = \int \frac{\partial \phi_{\text{xc}}}{\partial D_{kl}} \, dr = \int \sum_i \frac{\partial \phi_{\text{xc}}}{\partial n_i} \frac{\partial n_i}{\partial D_{kl}} \, dr, \quad (92)$$

where $n_i$ is used to collectively represent both of the local density variables, $n$ and $(\nabla n \cdot \nabla n)$. Consider as an example the geometric gradient (superscript $g$) of the XC contribution to
the linear response due to a perturbation $p$. We can write this compactly as

$$
K_{xc,kl}^{ep} = \int \left[ \frac{\partial^2 \epsilon_{xc}}{\partial \eta_l} \left( \frac{\partial \eta_l}{\partial D_{ax}} \right)^p + \frac{\partial^2 \epsilon_{xc}}{\partial \eta_l} \left( \frac{\partial \eta_l}{\partial D_{ax}} \right)^q \right] \mathrm{d}r.
$$

(93)

The working equations hidden behind this compact notation are rather involved already for an XC functional that depends only on two variables, $n$ and $(\nabla n \cdot \nabla n)$. Instead of presenting these lengthy equations we refer the reader to ref. 46 for explicit expressions of $K_{xc,kl}^{ep}$. Extending this functionality to more density variables (to accommodate spin polarization for instance) and to higher orders in geometric and electromagnetic perturbations clearly calls for automated recursive programming techniques. We note that formally also contributions arising from the changes in the grid when the nuclei move should be included in the KS-DFT contributions to the geometric derivatives. These contributions are in most cases ignored, though care must be exercised in order to ensure that the resulting geometric derivatives satisfy translational and rotational symmetry.204

We should point out that since genuine relativistic XC functionals that depend on the four-current are presently not available and because relativistic corrections to XC functionals have been found to have only little effect on calculated valence properties,205 206 it is common practice to use nonrelativistic functionals even in four-component codes, as done in this work: we always employ nonrelativistic functional derivatives also in the relativistic implementation, albeit evaluated using relativistic densities. We emphasize, however, that our implementation of the XC kernel derivatives are not limited to relativistic wave functions only,160 and in addition to also being applicable with nonrelativistic codes, it has also been used together with periodic boundary condition methods.208

4. Applications

We will in this section give some examples of molecular properties that are within reach using the different tools presented in the previous section. The selection of properties is not meant to be complete, and is primarily meant to illustrate the wide variety of properties that now can be calculated using analytic methods. The examples will largely be taken from work in our own laboratories during the last few years, with an emphasis on properties that previously have only to a limited extent been explored using analytic methods, that is, properties that either involve PDBS to higher order, or examples from the relativistic domain. The formalism presented in the previous section is applicable to both HF and KS-DFT, but we will for simplicity only give the working equations for the case of HF theory. The use of the XC-Fun library201 allows for an easy incorporation of the contributions from the XC functionals, and we will therefore not consider these explicitly here, and only in section 4.5 will we consider KS-DFT results.

4.1 Hyperpolarizabilities in the relativistic domain

Calculations of higher-order polarizabilities involving one-electron orbitals have been summarized in several excellent reviews,1 to which we refer the reader for further details, but has with a few exceptions151-153,209 largely been limited to the non-relativistic domain (excluding here for instance the use of effective core potentials in calculations of (hyper)polarizabilities).210 The formalism introduced in the previous section is applicable also to two- and four-component relativistic wave functions, and the expressions for the polarizability, the first and the second hyperpolarizabilities—that is, the second-, third- and fourth-order derivatives of the energy with respect to applied frequency-dependent electric fields $f_m$ associated with the frequency component $\omega_m$ can be written154,159

$$
K_{ijkl}^{pp} = \frac{\partial^2 \epsilon_{xc}}{\partial \eta_i \partial \eta_j} \left( \frac{\partial \eta_i}{\partial D_{ax}} \right)^p \left( \frac{\partial \eta_j}{\partial D_{ax}} \right)^p,
$$

(94)

$$
-\alpha_{ij}(\omega_1; \omega_2) = \epsilon_{xc}^{\omega_1 \omega_2} = \text{Tr} \epsilon_{xc}^{\omega_1 \omega_2},
$$

(95)

$$
-\beta_{ij}(\omega_1; \omega_2; \omega_3) = \epsilon_{xc}^{\omega_1 \omega_2 \omega_3} = \text{Tr} \epsilon_{xc}^{\omega_1 \omega_2 \omega_3},
$$

(96)

where energy conservation requires that $\omega_1 = -\sum_{m \geq 2} \omega_m$ and the subscripts $ijkl$ indicate the Cartesian component of the applied electric field. The expressions in eqn (94)–(96) could of course also be rewritten in order to take advantage of the $2n + 1$ rule.54,166 To illustrate the importance of relativistic effects on the hyperpolarizabilities, we report in Table 1 the second hyperpolarizability of hydrogen iodine (HI) for different optical processes as calculated using the four-component Dirac–Coulomb Hamiltonian, the spin-free (SF) four-component level of theory173,174 and the regular nonrelativistic Hamiltonian. The analysis is done in terms of the isotropically averaged second hyperpolarizability $\gamma$, defined as

$$
\gamma = \frac{1}{15} \sum_{i=x,y,z} \left[ \gamma_{ixx} + \gamma_{iyy} + \gamma_{iZZ} \right].
$$

(97)

We analyze the calculated second hyperpolarizabilities in terms of the relative importance of the scalar and spin–orbit effects to the observed relativistic corrections to the hyperpolarizabilities. All data have been taken from ref. 154.

We note from Table 1 that for low optical frequencies, the relativistic effects are in general rather small, being in most cases less than $5–10\%$, and dominated by the spin–orbit effects. Due to the dominance of the spin–orbit effects, which changes the excited-state spectrum of the molecule, the pole structure of the molecule changes significantly when spin–orbit effects are introduced,211 and this leads to a marked increase in the relativistic effects as we increase the optical frequencies. The perhaps most noticeable examples of these changes in the pole structure can be observed for the third-harmonic generation process $\gamma^{\omega_1 \omega_2 \omega_3}(-\omega_1; \omega, \omega_0)$ at a frequency of $\omega_0 = 0.1$ a.u., where the sign of the second hyperpolarizability differs between the non-relativistic and spin-free cases compared to the Dirac–Coulomb calculations due to the difference in pole structure with and without spin–orbit coupling in the calculations. Still, for all calculations at $\omega_0 = 0.1$ a.u. we are in the resonant region for this optical process, for which modifications to the theory presented in the previous section need to be introduced in order to obtain
numerically meaningful results, and such an approach has been presented by Kristensen et al.,212 building on the work of Norman and coworkers.213,214

4.2 Geometric derivatives of (hyper)polarizabilities: coherent anti-stokes Raman scattering and pure vibrational contributions to hyperpolarizabilities

There are several examples of analytic calculations of geometric derivatives of the frequency-dependent polarizabilities in the literature. Implementations of polarizability gradients at the HF level of theory have been presented by Quinet and Champagne,40,41 and by Rappoport and Furche at the KS-DFT level.43 We also note the recent extension of the linear scaling response formulation to the calculation of geometric derivatives of linear response functions and their residuals, including the polarizability gradient.46 Hyperpolarizability gradients have been presented at the HF level of theory by Quinet and Champagne.

The scheme of Quinet and Champagne40,42 uses the $2n + 1$ rule to calculate the polarizability derivatives. In this way, only first-order-perturbed wave functions need to be determined, at the cost that these first-order-perturbed wave functions need to be determined for all the applied perturbations. In the case of perturbations involving nucleus-dependent properties, such as nuclear displacements or nuclear magnetic moments, the number of perturbed wave functions that need to be determined increases with increasing molecular size, whereas the number of electric field perturbations remain constant. As such, resorting to the in general weaker $n + 1$ rule, as described in the previous section, will be advantageous, as utilized both by Rappoport and Furche,43 by Coriani et al.,46 and in our recent works.45,215

In the notation of our previous section, the gradients of the dipole moment, polarizability and first hyperpolarizability can be written as

$$Q^{\alpha} = \frac{dQ^{\alpha}}{dF_{\alpha}} = \psi^{\alpha} + \text{Tr} V\psi^{\alpha} D$$

(98)

where we have used $g$ as a superscript to indicate a geometric derivative, and where we have not indicated the frequency components of the electric field for ease of notation. We have in these equations also utilized that $T^g$ vanishes since only static fields are associated with the geometric derivatives.

In addition to determining conventional Raman spectroscopy,43 the polarizability gradients are also important in determining Coherent Anti-Stokes Raman Scattering

Table 1 Average electronic second hyperpolarizabilities $\gamma^i$ for HI evaluated at several frequencies at the Dirac–Coulomb equilibrium distance of 3.0318 bohr (all values in a.u.; NR: nonrelativistic; SF: spin–free modified Hamiltonian; DC: Dirac–Coulomb Hamiltonian; SR: scalar relativistic (SF–NR); SO: spin–orbit coupling effect). For information about the basis set, see ref. 154

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<td>12897.7</td>
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<td>14103.8</td>
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<td>1.4%</td>
<td>1.5%</td>
<td>1.7%</td>
<td>2.0%</td>
</tr>
<tr>
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<td>4.2%</td>
<td>4.4%</td>
<td>4.8%</td>
<td>5.4%</td>
</tr>
<tr>
<td>SR + SO</td>
<td>5.4%</td>
<td>5.6%</td>
<td>6.0%</td>
<td>6.5%</td>
<td>7.1%</td>
</tr>
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<td>6.7%</td>
<td>8.2%</td>
<td>10.3%</td>
</tr>
<tr>
<td>$\gamma^i(-2\omega, 0, -\omega, 0)$</td>
<td></td>
<td></td>
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<tr>
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<td>13182.7</td>
<td>16044.5</td>
<td>21935.2</td>
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<tr>
<td>SF</td>
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<td>16782.0</td>
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<td>39431.1</td>
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<tr>
<td>DC</td>
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<td>13999.1</td>
<td>17274.5</td>
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<td>42860.2</td>
</tr>
<tr>
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<td>1.6%</td>
<td>2.1%</td>
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<td>9.0%</td>
</tr>
<tr>
<td>SO</td>
<td>4.1%</td>
<td>4.6%</td>
<td>5.5%</td>
<td>8.4%</td>
<td>9.5%</td>
</tr>
<tr>
<td>SR + SO</td>
<td>5.5%</td>
<td>6.2%</td>
<td>7.7%</td>
<td>11.6%</td>
<td>18.5%</td>
</tr>
<tr>
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<td>26781.8</td>
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<tr>
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<td>12.0%</td>
</tr>
<tr>
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<td>5.4%</td>
<td>6.3%</td>
<td>50.2%</td>
<td>-239.8%</td>
</tr>
<tr>
<td>SR + SO</td>
<td>5.7%</td>
<td>7.4%</td>
<td>10.6%</td>
<td>48.6%</td>
<td>-227.8%</td>
</tr>
</tbody>
</table>

* During the iterative solution of the response equations we have observed that the matrix of the reduced system has negative eigenvalues, indicating that we have passed the first pole of the system. The lowest dipole-allowed Hartree–Fock excitation energy of HI is 0.219 $E_0$(NR), 0.217 $E_0$(SF), and 0.193 $E_0$(DC) using the respective equilibrium distances and Hamiltonians.
(CARS), a four-wave mixing process in which the Raman scattering is enhanced by applying two different optical frequencies such that their frequency difference matches a vibrational excitation and thus enhances the scattering process. It can be shown that the CARS signal is given by the expression

$$|\gamma|^2 = \left| (\gamma_R^R + i\gamma_I^R) + \gamma_e \right|^2 = \left( \gamma_R^R \right)^2 + 2\gamma_R^R \gamma_e + (\gamma_e)^2 + (\gamma_I^R)^2, $$

(101)

with $\gamma_e$ being the electronic second hyperpolarizability, being here an approximation to the full non-resonant contribution, whereas the dominating contribution is due to the resonant CARS signal, split into its real $\gamma_R^R$ and imaginary $\gamma_I^R$ components, and determined by the expression

$$\gamma_{i,j,k,l}^{\text{CARS Res}}(-\omega_a; \omega_1, -\omega_2, \omega_3) \approx 2 \sum_v \left[ \frac{\langle 0 | z_v(\omega_3)|v\rangle \langle v | z_v(\omega_1) | 0 \rangle}{\omega_\alpha - (\omega_1 - \omega_2) + i\epsilon} \right]$$

$$+ \frac{\langle 0 | z_v(\omega_3)|v\rangle \langle v | z_v(\omega_1) | 0 \rangle}{\omega_\alpha - (\omega_1 - \omega_2) + i\epsilon}, $$

(102)

where $\omega_\alpha = 2\omega_3 - \omega_1 - \omega_2$, $\epsilon$ is a small number introduced to avoid divergencies in the response function at resonant energies and which can be shown to be related to the lifetime of the excited state, 2 and where $|v\rangle$ corresponds to a vibrationally excited state of the electronic ground state, and $h\omega_\alpha$ is the corresponding vibrational excitation energy.

In addition to enhancing the scattering cross sections observed in conventional Raman spectroscopy, an added benefit of CARS is that it can reduce the problems due to fluorescence, and this has made CARS an unique and powerful tool for probing the structure and function of a wide range of materials. Despite the fact that the theory of CARS has been well established for a long time, only two ab initio CARS studies have been presented in the literature. An example of the differences in the CARS and Raman spectra that can be observed, and the ability of theory to reproduce the observed scattering intensities, is given in Fig. 1 for the 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) molecule. More details about the calculations and the analysis of the spectrum can be found in ref. 216.

The polarizability and hyperpolarizability gradients, as well as the dipole gradients, also enter in the expression for so-called pure vibrational contributions to the hyperpolarizabilities. In the language of the sum-over-states expressions for these properties, these contributions arise from virtual excitations in the vibrational domain of the total molecular wave function instead of in the electronic domain as is the case for the electronic hyperpolarizabilities in eqn (94)–(96). A perturbation theory approach for calculating the pure vibrational corrections to hyperpolarizabilities was presented by Bishop and Kirtman. Their analysis showed that the pure vibrational contributions could be calculated from products of geometric derivatives of static (hyper)polarizabilities of lower order than the hyperpolarizability of interest. In the so-called double-harmonic approximation, in which we represent the vibrational wave function by a harmonic oscillator and only include the linear dependence of the (hyper)polarizabilities on the nuclear displacements, the expressions for the pure vibrational contributions to $x, y, z$ and $\beta, \gamma$ can be written

$$x_{ij}^x = \frac{1}{2} \sum g_{ij} \frac{\partial \mu_i}{\partial Q_g} \frac{\partial \mu_j}{\partial Q_g}, $$

(103)

$$y_{ij}^x = \frac{1}{2} \sum g_{ij} \frac{\partial \mu_i}{\partial Q_g} \frac{\partial \mu_j}{\partial Q_g}, $$

(104)

$$\gamma_{ijkl}^x = \frac{1}{2} \sum g_{ijkl} \frac{\partial \mu_i}{\partial Q_g} \frac{\partial \mu_j}{\partial Q_g}, $$

(105)

where $g_{ijkl}$ denotes the possible permutations of the dipole moment components and their associated frequencies, $Q_g$ denotes a normal mode, and the frequency terms are defined as

$$\omega_g^{+s} = \left[ \omega_g^2 - \omega_e^2 \right]^{-1}, $$

(106)

$$\omega_g^{+23} = \left[ \omega_g^2 - \omega_e^2 + \omega_2 \omega_3 \right]^{-1}. $$

(107)

The importance of the pure vibrational contributions to the nonlinear optical properties, in particular static polarizabilities, is well documented, and we refer to the reviews by Bishop and Bishop and Norman for an account of calculations of pure vibrational contributions.

Our formulation of the pure vibrational contributions in terms of the density matrix in the AO basis allows us to calculate these pure vibrational contributions using large basis sets for much larger systems than previously studied theoretically. In Table 2, we report the static electronic and non-resonant Raman spectra, which is taken from ref. 217. Figure reproduced from ref. 216 with permission from Elsevier.

Fig. 1 (Color online) Calculated CARS and non-resonant Raman spectra for RDX at 532 nm. The inset shows the experimental CARS and non-resonant Raman spectra, which is taken from ref. 217. Figure reproduced from ref. 216 with permission from Elsevier.
results in Table 2 actually being exceptionally large, whereas for the first and second hyperpolarizabilities, the pure vibrational contributions may actually dominate over the electronic hyperpolarizabilities for static electric fields. We emphasize that the importance of the pure vibrational contributions are in general significantly damped when optical frequencies are considered, to the extent that they often more or less vanish, as is most often the case for instance for third-order harmonic generation $\gamma(-3\omega; \omega, \omega, \omega)$.\textsuperscript{218}

### 4.3 Raman optical activity

Raman optical activity (ROA) is the chiral analogue of Raman spectroscopy, in which the observed quantity is the differential scattering of left and right circularly polarized light. For chiral molecules, ROA is a unique fingerprint method that in addition to providing the detailed spectroscopic information obtained in all vibrational spectroscopies also provides information about the absolute configuration of the molecule,\textsuperscript{222} as the ROA spectrum of two enantiomers are mirror images of each other. When used in conjunction with \textit{ab initio} methodology to assign the observed ROA spectrum with a specific enantiomer,\textsuperscript{222,223} ROA and the closely related technique of vibrational circular dichroism (VCD) represent some of the most powerful methods for determining structures and absolute configurations of chiral molecules in their native environments.\textsuperscript{222,224–226} One of the most exciting examples of the powers of ROA as a spectroscopic method for determining absolute configuration was the study by Haesler \textit{et al.} of the absolute configuration of chirally deuterated ($\text{R}$)-[\text{H}, \text{H}_2, \text{D}_3]-neopentane.\textsuperscript{223}

The theory for ROA and the theoretical prediction of the effect was made by Atkins and Barron\textsuperscript{227} and by Barron and Buckingham,\textsuperscript{228} and the first experimental observation of the effect was made in 1973 by Barron, Bogaard and Buckingham,\textsuperscript{229} independently confirmed the year after by Hug \textit{et al.} We will not here discuss the different forms of the circular intensity differences for the scattered light observed in the many different experimental setups of ROA, and the corresponding ROA invariants, referring instead to reviews discussing these topics.\textsuperscript{231,232} In the context of this perspective, it suffices to note that what is needed from an \textit{ab initio} calculation is the molecular force field and the geometric gradients of the polarizability, the mixed electric dipole–electric quadrupole polarizability and the mixed electric dipole–magnetic dipole polarizability. The first analytic calculations of ROA spectra were presented by Liégeois, Ruud and Champagne using the $2n + 1$ rule and conventional basis sets.\textsuperscript{44} We recently extended the theory to also include the effects of LAOs and using the $n + 1$ rule.\textsuperscript{233} The mixed electric dipole–electric quadrupole polarizability is easily obtained from eqn (94) by replacing one of the electric dipole operators with the electric quadrupole operator

$$Q^{bf} = \text{Tr} \nabla h \mathbf{D}',$$  

whereas the mixed electric dipole–magnetic dipole polarizability is given as (including the effects of LAOs)

$$Q^{bf} = \text{Tr} \mathbf{D}^{bf} + \text{Tr} \mathbf{h}^{bf} \mathbf{V}^{bf} - \frac{1}{2} \mathbf{T}^{bf} + \mathbf{G}^{bf}(\mathbf{D}) \mathbf{D}' - \text{Tr} \mathbf{S}' \mathbf{W}.'$$

However, we need the gradients of these polarizabilities, the polarizability gradient being given in eqn (99), whereas the expression for the electric-dipole–electric-quadrupole polarizability in this framework is given as

$$Q^{bf} = \text{Tr} \nabla h \mathbf{D}' + \text{Tr} \mathbf{h} \mathbf{V} - \frac{1}{2} \mathbf{T} + \mathbf{G}(\mathbf{D}) \mathbf{D}' - \text{Tr} \mathbf{S} \mathbf{W}.'$$

where we have used the superscript $q$ to indicate the traceless quadrupole moment operator. For the electric–magnetic dipole polarizability, additional terms arise due to the use of LAOs, giving\textsuperscript{233}

$$Q^{bf} = \text{Tr} \mathbf{V}^{bf} \mathbf{D}' + \text{Tr} \mathbf{G}(\mathbf{D}) \mathbf{D}' - \text{Tr} \mathbf{S} \mathbf{W}.'$$

where $f^*$ indicate that we for convenience are considering the positive frequency-component of the electric field $c_o f = -c_o f$.

The availability of an analytic approach for calculating ROA spectra can be expected to be as important for the future development of this spectroscopy as the availability of reliable VCD calculations turned out to be.\textsuperscript{222} The use of the $n + 1$ rule also makes the calculations very efficient and much less expensive than for instance the determination of the molecular force field, as only 45 perturbed densities need to be determined independently of the size of the molecule.\textsuperscript{233} This has allowed for calculations on fairly large systems, such as the trimethylsilyl ether of menthol\textsuperscript{234} (the trimethylsilyl ether here ensures that the menthol molecule exists primarily in a single conformation), see Fig. 2. Analytic approaches also make it possible to simulate ROA spectra by sampling several hundred structures obtained by taking snapshots from molecular dynamics simulations, including in the calculations both the solute and the nearest solvation shell(s), as has been done for instance for lactamide by Hopmann \textit{et al.}\textsuperscript{235}

### 4.4 Nonlinear birefringence: electric-field-gradient-induced birefringence

Chiroptical properties such as ROA only occur for chiral molecules—that is, molecules which are not superimposable on their mirror image—due to the fact that the refractive index of such molecules differs for the right and left circularly polarized components of the light. More generally, we refer to phenomena in which there is a difference in the refractive index for two different components as a birefringence,\textsuperscript{236} in the particular case of the anisotropy with respect to right and left circularly polarized components of the refractive index we refer to this as a \textit{circular} birefringence, of which the most common examples are optical rotation\textsuperscript{30,31} and circular dichroism.\textsuperscript{82} However, we can also observe differences in the components of the refractive index perpendicular and parallel to an externally applied field, and such birefringences are in general referred to as \textit{linear} birefringences. Being defined with respect to the axes of an externally applied field, linear birefringences can be observed for any kind of molecules,
Table 2 Polarizabilities of push-pull aldehydes, C3H3NO, C9H7NO and C25H33NO (IIIa, IIIb and IIIc). Data taken from ref. 215

<table>
<thead>
<tr>
<th>Electronic polarizabilities</th>
<th>IIIa</th>
<th>IIIb</th>
<th>IIIc</th>
</tr>
</thead>
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<td>$\mu_e$</td>
<td>3.2204</td>
<td>3.7938</td>
<td>4.2012</td>
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<tr>
<td>$d'$</td>
<td>163.1</td>
<td>363.5</td>
<td>713.2</td>
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<td>$3\beta_{zzz}/s$</td>
<td>1574</td>
<td>7802</td>
<td>23000</td>
</tr>
<tr>
<td>$\gamma'/5$</td>
<td>7.688</td>
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<td>76.56</td>
</tr>
<tr>
<td>$\gamma''_{zzzz}/5$</td>
<td>5.334</td>
<td>$10^4$</td>
<td>70.93</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Vibrational polarizabilities</th>
<th>IIIa</th>
<th>IIIb</th>
<th>IIIc</th>
</tr>
</thead>
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<tr>
<td>$\beta_{zzz}$</td>
<td>61.3</td>
<td>108.6</td>
<td>192.2</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>5284</td>
<td>32.251</td>
<td>103.154</td>
</tr>
<tr>
<td>$3\beta_{zzz}/s$</td>
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<td>103.173</td>
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<tr>
<td>$\gamma'/5$</td>
<td>12.62</td>
<td>$10^4$</td>
<td>278.60</td>
</tr>
<tr>
<td>$\gamma''_{zzzz}/5$</td>
<td>13.76</td>
<td>$10^4$</td>
<td>262.80</td>
</tr>
</tbody>
</table>

$^a$ Sadlej basis set. $^b$ In the dominant component approximations: $\mu_\parallel = \frac{1}{3} \mu_{zzz}$ and $\gamma = \frac{1}{3} \gamma_{zzzz}$. The dipole moment is along the $z$ axis.

and the most well-known examples of linear birefringences refer to experiments in which one measures the refractive index parallel and perpendicular to an electric field (the Kerr (or electro-optic) effect).\(^\text{237–239}\) Other examples of linear birefringences are Buckingham birefringence arising due to an external electric field gradient\(^\text{240}\) and the Cotton–Mouton effect,\(^\text{9,10}\) in which an external magnetic field is applied, as well as the Jones birefringence observed when both an electric and a magnetic field are applied.\(^\text{7,8}\) For completeness, we note that there also exists a third birefringence, namely axial birefringence, of which magneto- and chiral birefringence is the most common example.\(^\text{241,242}\)

Birefringences are in general determined by several mixed (hyper)polarizabilities. When magnetic fields are involved, LAOs have to be used in order to obtain gauge-origin independent results. Buckingham and Jones birefringences and the Cotton–Mouton effect have all been treated using the theory presented in the previous section,\(^\text{243,245}\) but we will here only discuss the Buckingham birefringence, with the goal to illustrate the general features of birefringence calculations, as well as the powers of the framework presented in the previous section. We have chosen to use Buckingham birefringence in part to avoid too complicated expressions, in part because of its importance as a method for determining molecular quadrupole moments, and because we can illustrate the importance of using LAOs in order to obtain reliable results that are gauge-origin independent.

In the presence of an externally applied electric field gradient, an anisotropy in the refractive index is observed, which for an ideal gas is given by (in SI units, constant pressure)\(^\text{240}\)

$$\Delta n = n_x - n_y = \frac{N_A}{15V_m c_0} \left( \frac{3\nabla E}{2V_m} mQ(\omega, T) \right), \quad (112)$$

and

$$mQ(\omega, T) = \frac{2N_A}{45c_0} s, \quad (113)$$

where $N_A$ is Avogadro’s number, $V_m$ is the molar volume, $\nabla E$ is the field gradient with $\nabla E = -\nabla E_{XX} = -\nabla E_{YY}$; $\nabla E_{ZZ} = 0$, and $c_0$ is the vacuum permittivity. In this expression, the light is assumed to propagate along the $Z$ direction. The molecular function $s$ is for dipolar molecules given as\(^\text{246}\)

$$s = b(\omega) + \frac{1}{kT} \left\{ \Theta_{ij} \gamma_j(-\omega; \omega) - \mu_i [A_{ij}(-\omega; \omega)$$

$$+ \frac{5}{\omega} \epsilon_{ijk} G'_{ijk}(-\omega; \omega)] \right\}, \quad (114)$$

where $\Theta_{ij}$ is the traceless quadrupole moment operator, $A_{ij}$ the mixed electric dipole–electric quadrupole polarizability eqn (108), $G'_{ijk}$ the mixed electric dipole–magnetic dipole polarizability eqn (109), and the temperature-independent contribution is given as

$$b(\omega) = B_{ijk}(-\omega; \omega, 0) - B_{ijk}(-\omega; \omega, 0) - \frac{5}{\omega} \epsilon_{ijk} J_{ijk}'(-\omega; \omega, 0), \quad (115)$$

In this equation, $\epsilon_{ijk}$ is the Levi–Civita antisymmetric tensor and implicit summation over repeated indices is employed. In the expression for $b(\omega)$ we have introduced the mixed polarizabilities

$$B_{ijk}(-\omega; \omega, 0) = \langle \langle \hat{\mu}_i; \hat{\mu}_j; \hat{\Theta}_kl \rangle \rangle_{\omega, 0}, \quad (116)$$

$$B_{ijk}(-\omega; \omega, 0) = \langle \langle \hat{\mu}_i; \hat{\Theta}_jk; \hat{\mu}_l \rangle \rangle_{\omega, 0}, \quad (117)$$

$$J_{ijk}'(-\omega; \omega, 0) = \langle \langle \hat{\mu}_i; \hat{n}_j; \hat{n}_k \rangle \rangle_{\omega, 0}. \quad (118)$$

Of these three tensors, $B_{ijk}(-\omega; \omega, 0)$ and $B_{ijk}(-\omega; \omega, 0)$ are obtained straightforwardly from eqn (95), exchanging one of the dipole operators with the traceless quadrupole operator. Due to the use of London AOs, the expression for $J_{ijk}'(-\omega; \omega, 0)$ becomes somewhat more complicated, and we can write it as\(^\text{243}\)

$$Q_{\omega\omega\omega\omega} = \text{Tr} V_{\omega\omega} D_{\omega\omega} + \text{Tr} V_{\omega\omega} D_{\omega\omega}$$

$$+ \text{Tr} [h_{\omega\omega} + V_{\omega\omega} - \frac{i}{2} T_{\omega\omega} + G_{\omega\omega}(D)] D_{\omega\omega}, \quad (119)$$

where

$$Q_{\omega\omega\omega\omega} = J_{ijk}'(-\omega; \omega, 0) = \langle \langle \hat{n}_i; \hat{n}_j; \hat{n}_k \rangle \rangle_{\omega, 0}. \quad (120)$$

We illustrate in Table 3 the importance of LAOs when calculating the temperature-independent contribution to the Buckingham birefringence, $b(\omega)$ of furan. We note in particular that the LAO results are independent of whether we place the gauge origin in the center of mass of the molecule, or at the oxygen atom in the furan ring, in contrast to when LAOs are not employed. However, more important is the much faster basis convergence observed with the LAOs, the LAO results all being less than 2% off the results obtained with the aug-cc-pVQZ basis set, whereas the non-LAO results differ by more than 20% for the aug-cc-pVDZ basis set, and are still off the aug-cc-pVQZ LAO result by 3% with the aug-cc-pVQZ basis set. The improvements in basis set dependence obtained with LAOs for the observable temperature-independent
Fig. 2 Experimental and computed ROA backscattering spectra of the trimethylsilyl ether of menthol. From top to bottom: experimental spectrum, computed spectra with parameters as indicated. A linear correction has been applied to the calculated frequencies so that a shift of 0 cm⁻¹ results for 300 cm⁻¹ and of -32 cm⁻¹ for 1600 cm⁻¹. The experimental data were recorded as follows: exposure time 60 min, laser power at sample 400 mW, exciting wavelength 532 nm, instrumental resolution 7 cm⁻¹. The curve has been slightly smoothed with the second-order symmetric five-point Savitzky-Golay filter, see ref. 234.

contribution to the Buckingham birefringence are thus comparable to that observed for magnetizabilities¹²⁵ and rotational g tensors.¹²⁶,²⁴⁴ For a comparison of the calculated results with experimental observations of the Buckingham birefringence of furan, fluorobenzene and naphthalene, we refer to ref. 243.

### 4.5 Higher-order polarizabilities at the KS-DFT level of theory

Finally, in order to illustrate how the formalism presented in the previous section for the open-ended response theory approach in combination with the use of automatic differentiation allow us to calculate high-order response functions also at the KS-DFT level, we report in Table 4 the polarizability and the first-, second-, and third-order hyperpolarizabilities in hydrogen fluoride, previously reported in ref. 160. The third-order hyperpolarizability \( \delta (-4\omega; \omega, \omega, \omega, \omega) \) can be calculated based on the same formulas as discussed in section 4.1, that is:

\[
\delta_{ijklm}(-\omega_1; \omega_1, \omega_2, \omega_3, \omega_4) = \mathbf{Q}_{ijklm}^{(0)} \mathbf{D}_{ijklm}^{\omega_1 \omega_2 \omega_3 \omega_4},
\]

We present the numbers for different optical frequencies and for both HF wave functions and KS-DFT using the local-density approximation. The XCFun library²⁰³ has implemented a large variety of different functionals, including GGA functionals, hybrid functionals, and meta-GGA functionals, but we do not

Table 3 Calculated results for the hyperpolarizability tensor averages and for the temperature independent contribution \( b(\omega) \) to Buckingham birefringence of furan. A wavelength of 632.8 nm is employed in the calculations. All quantities are given in atomic units. “LAO” and “NoLAO” indicate the use of perturbation dependent London Orbitals or conventional basis sets, respectively.

<table>
<thead>
<tr>
<th>Basis</th>
<th>Origin</th>
<th>( B )</th>
<th>( B )</th>
<th>( \beta' )</th>
<th>( \beta' )</th>
<th>( h )</th>
<th>( h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVDZ</td>
<td>CM</td>
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<td>LAO</td>
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<tr>
<td></td>
<td>O</td>
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<td>-9541.9</td>
<td>24.92</td>
<td>30.98</td>
<td>NoLAO</td>
<td>LAO</td>
</tr>
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<td>aug-cc-pVTZ</td>
<td>CM</td>
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<td>-10059.6</td>
<td>28.95</td>
<td>31.16</td>
<td>NoLAO</td>
<td>LAO</td>
</tr>
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<td>O</td>
<td>-10405.5</td>
<td>-10258.5</td>
<td>28.54</td>
<td>30.89</td>
<td>NoLAO</td>
<td>LAO</td>
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<tr>
<td>aug-cc-pVQZ</td>
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<td>-10500.3</td>
<td>-10354.5</td>
<td>30.26</td>
<td>31.17</td>
<td>NoLAO</td>
<td>LAO</td>
</tr>
<tr>
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<td>O</td>
<td>-10726.7</td>
<td>-10563.6</td>
<td>29.93</td>
<td>30.92</td>
<td>NoLAO</td>
<td>LAO</td>
</tr>
</tbody>
</table>

Table 4 Components of the static and frequency-dependent polarizability, and the first, second, and third hyperpolarizabilities of FH calculated using the q-aug-cc-pVTZ basis set (all numbers in atomic units; all perturbing dipole operators carry the same frequency, 0, 0.06562 a.u., or 0.072 a.u.; \( R_e = 1.7328 \) bohr; the direction of the positive z axis is from F to H).

<table>
<thead>
<tr>
<th>( \omega = 0 )</th>
<th>( \omega = 0.06562 ) a.u.</th>
<th>( \omega = 0.072 ) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha(x,x) )</td>
<td>4.495</td>
<td>5.930</td>
</tr>
<tr>
<td>( \alpha(z,z) )</td>
<td>5.759</td>
<td>6.854</td>
</tr>
<tr>
<td>( \beta(x,x,x) )</td>
<td>-0.5087</td>
<td>-2.329</td>
</tr>
<tr>
<td>( \beta(z,z,x) )</td>
<td>-0.5087</td>
<td>-2.329</td>
</tr>
<tr>
<td>( \gamma(x,x,x) )</td>
<td>335.9</td>
<td>1148.</td>
</tr>
<tr>
<td>( \gamma(z,z,z) )</td>
<td>96.87</td>
<td>309.6</td>
</tr>
<tr>
<td>( \gamma(z,z,x) )</td>
<td>96.87</td>
<td>309.6</td>
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<tr>
<td>( \gamma(z,z,z) )</td>
<td>279.6</td>
<td>636.1</td>
</tr>
<tr>
<td>( \delta(x,x,x,x) )</td>
<td>111.3</td>
<td>592.6</td>
</tr>
<tr>
<td>( \delta(z,x,x,x) )</td>
<td>111.3</td>
<td>592.6</td>
</tr>
<tr>
<td>( \delta(x,z,x,z) )</td>
<td>111.3</td>
<td>592.6</td>
</tr>
<tr>
<td>( \delta(z,z,z,z) )</td>
<td>75.95</td>
<td>1618.</td>
</tr>
<tr>
<td>( \delta(z,z,z,z) )</td>
<td>-1484.2</td>
<td>-2079.</td>
</tr>
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</table>
report these results as our study in ref. 160 showed that even though the results are stable with respect to the differentiation of the XC functionals, standard grids used in the integration of XC functionals and their derivatives are not designed to treat densities that are very diffuse, as is the case when higher-order polarizabilities are considered, see Fig. 3. Indeed, we have observed that these grid instabilities may manifest themselves already for first hyperpolarizabilities. Further work needs to be done in order to design grids that can accurately integrate also very diffuse perturbed densities.

We note from Table 4 that electron correlation as described by the LDA functional leads to an increase in the polarizability and hyperpolarizabilities, and more so the higher the optical frequency and the higher the optical process. The increased dispersion at the LDA level is due to the fact that LDA in general will give too low excitations energies, whereas HF in general gives too large excitation energies, and we would expect the dispersion to be somewhat in between that observed for HF and LDA. Thus, with the development of grids that allow for an accurate integration of highly perturbed densities, we are able to treat correlation effects on higher-order polarizabilities in an approximate manner using suitable XC kernels. The lack of reliable experimental data for the higher-order polarizabilities to which we can compare our results makes it important to benchmark the results obtained with different functionals against for instance the open-ended coupled-cluster response approach of Hättig et al.\textsuperscript{79,80}

5. Summary

We have in this perspective given an overview of the efforts in our groups during the last few years to develop a general and flexible framework for calculating molecular properties of arbitrary order for time- and perturbation-dependent basis sets. By formulating the quasienergy derivative theory in terms of the density matrix in the AO basis, the approach allows us to use the same structure, and indeed the same library of routines, for non-relativistic and two- and four-component relativistic self-consistent field wave functions. The differences in the Hamiltonian and in the representation of the wave function are contained within the routines that calculate the molecular self-consistent-field energy and solve the linear sets of equations that determine the perturbed densities to different orders. The versatility of the approach is illustrated by the fact that the same response routines have been combined with both the AO- and MO-based versions of the Dalton program\textsuperscript{158,168,193} as well as with the relativistic two- and four-component program dirac.\textsuperscript{182}

We have in this perspective focused on molecular properties that can be expressed as derivatives of the quasienergy. The approach can also be generalized to consider transition densities,\textsuperscript{159} allowing for the determination of transition moments and excited-state properties, and in this manner we can also determine excited-state gradients and Hertzberg–Teller factors,\textsuperscript{46} as well as the $B$ term of magnetic circular dichroism.\textsuperscript{37} The formalism has also been extended to resonant regions.\textsuperscript{212}

In order to obtain a flexible toolbox for the calculation of molecular properties of arbitrary order, and in particular when perturbation-dependent basis sets are involved, we also need flexible one- and two-electron integral programs, as described in this perspective. Our scheme for calculating one-electron integral and their geometric derivatives allows us to compute any kind of integral occurring in the field of higher-order molecular properties. We have not discussed the evaluation of the magnetic-field derivatives of these one-electron integrals, but this will largely follow the strategy used for the magnetic-field derivatives of the two-electron integrals, discussed in section Fig. 3 BLYP XC energy density of the FH molecule (top panel) and $\mathbf{v}^\text{BLYP}$ of eqn (26) of ref. 160 (bottom panel; all perturbations are static and parallel to the molecular axis; q-aug-cc-pVTZ). The color intensity is proportional to the respective absolute value. The numerical integration grid points are represented as dots which "radiate" from the atom centers at (0, 0, 0) bohr and (0, 0, 1.7328) bohr (dimensions: 24 x 24 bohr). Reprinted with permission from ref. 160. Copyright 2010 American Chemical Society.
3.3. Other extensions that we are working on is the inclusion of effective core potential and model core potential integrals as well as their geometric and magnetic-field derivatives.

We have discussed a novel approach for the calculation of derivatives of complicated quantities, in particular the derivatives of the exchange-correlation functional, using automatic differentiation. Despite the limited use of automatic differentiation in quantum chemistry to date, we believe this is an approach that offers many advantages and that can be used for a wide variety of problems in quantum chemistry, leading both to more compact but also more flexible code, which in turn should reduce the time used on implementing new computational methodology, allowing researchers to easily test new ideas without any limitations on the calculations that may be done using the code.

The main purpose of developing this very general computational toolbox for evaluating molecular properties is of course to apply it to calculate properties of experimental interest. Two fields that to a limited extent have been explored by computational means, are nonlinear vibrational spectroscopies, including here also anharmonicities in vibrational spectroscopy, as well as molecular properties in the relativistic domain. Using the general toolbox presented here, we believe quantum chemistry is now in a position to make important contributions to both of these fields.

Acknowledgements

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