

Lawrence Berkeley National Laboratory

Recent Work

Title

The Chronus Quantum software package

Permalink

<https://escholarship.org/uc/item/36f1p562>

Journal

Wiley Interdisciplinary Reviews: Computational Molecular Science, 10(2)

ISSN

1759-0876

Authors

Williams-Young, DB
Petrone, A
Sun, S
[et al.](#)

Publication Date

2020-03-01

DOI

10.1002/wcms.1436

Peer reviewed

The Chronus Quantum (ChronusQ) Software Package

David B. Williams–Young^{abc}, Alessio Petrone^d, Shichao Sun^b,
Torin F. Stetina^b, Patrick Lestrangle^b, Chad E. Hoyer^b,
Daniel R. Nascimento^e, Lauren Koulias^b, Andrew Wildman^b,
Joseph Kasper^b, Joshua J. Goings^f, Feizhi Ding^g,
A. Eugene DePrince III^e, Edward F. Valeev^h, Xiaosong Li^{bi}

Article Type:

Software Focus

Abstract

The Chronus Quantum (ChronusQ) software package is an open source (under the GNU General Public License v2) software infrastructure which targets the solution of challenging problems that arise in *ab initio* electronic structure theory. Special emphasis is placed on the consistent treatment of time dependence and spin in the electronic wave function, as well as the inclusion of relativistic effects in said treatments. In addition, ChronusQ provides support for the inclusion of uniform finite magnetic fields as external perturbations through the use of gauge-including atomic orbitals (GIAO). ChronusQ is a parallel electronic structure code written in modern C++ which utilizes both message passing (MPI) and shared memory (OpenMP) parallelism. In addition to the examination of the current state of code base itself, a discussion regarding ongoing developments and developer contributions will also be provided.

^aComputational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720

^bDepartment of Chemistry, University of Washington, Seattle, WA, 98195, United States

^cCorresponding Author: dbwy@lbl.gov

^dDipartimento di Scienze Chimiche, Universit di Napoli Federico II, Complesso Universitario di M.S. Angelo, via Cintia, I-80126 Napoli, Italy

^eDepartment of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

^fDepartment of Chemistry, Yale University, 225 Prospect Street, New Haven, CT, 06520, United States

^gDivision of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, 91125, United States

^hDepartment of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States

ⁱCorresponding Author: xqli@uw.edu

INTRODUCTION

The development of the Chronus Quantum (ChronusQ) software package [1] began in the research group of Xiaosong Li at the University of Washington in the beginning of 2014. The primary purpose of ChronusQ at that time was to serve as an outlet for the dissemination of some of the more “unconventional” electronic structure method development taking place in the group. Chief among these developments was methodological experimentation in the fields of time-dependent and relativistic electronic structure theory, and specifically at their intersection. Over the years, ChronusQ has received contributions from many developers, and new and exciting functionality continues to be added to its code base to this day. ChronusQ is *free* software released under the GNU General Public License (v2), and is made publicly available at <http://www.chronusquantum.org>. In this context, *free* software is meant to indicate that ChronusQ is *gratis*, as well as the fact that it grants its recipients the freedom to use, modify and redistribute the code base under the same license.

The set of electronic structure methods implemented in the ChronusQ program spans both the novel, and the tried and tested. Contemporary software which implement similar pieces of quantum chemistry functionality include the ReSpect [2], DIRAC [3], DALTON [4], and BAGEL [5] programs. However there are a number of electronic structure methods implemented in ChronusQ which are, at the time that this article has been written and to the best of the authors’ knowledge, not currently available in any other public, open source quantum chemistry codes. These methods will be highlighted in the main text.

As the name might imply (*Chronus* being the latinization of *Time* personified in Greek mythology), the core of the functionality in ChronusQ centers around time-dependent electronic structure theory. However, it is through the lens of time-dependent phenomena that ChronusQ also provides a slew of related capabilities such the treatment of electronically excited states and molecular properties. ChronusQ provides functionality to solve time-dependent electronic structure problems both in the time and frequency domains. In conjunction with the time-dependent electronic structure methods, special emphasis is placed on the treatment of electronic spin throughout the code base, specifically in the context of broken spin–symmetry solutions. As such, all of the electronic structure methods implemented

in ChronusQ fully support the use of two-component spinor wave functions. In addition to these core functionalities, ChronusQ supports a number of complementary features which are not typically found in general purpose quantum chemistry software. Relativistic effects are supported throughout the code through the use of the exact two-component (X2C) method [6–11]. Magnetic fields may also be added as an external perturbation through the use of gauge including atomic orbitals (GIAO) [12–18]. All electronic structure methods implemented in ChronusQ are based on the linear combination of atomic orbitals (LCAO) paradigm to construct the electronic wave function using contracted Gaussian-type orbital (CGTO) basis set expansions. Both generally contracted and segmented CGTO basis sets are supported. ChronusQ is a single-reference quantum chemistry code which utilizes single Slater determinant descriptions of the ground state electronic wave function based on either Hartree-Fock (HF) or Kohn-Sham density functional theory (KS). Using the Slater determinant as a reference wave function, ChronusQ also supports various post-SCF methods such as the particle hole [19–21] and particle particle [22–24] random phase approximations. Additionally, the development of many body methods, such as coupled cluster theory [25], are currently underway.

Since its inception, the primary design goal of ChronusQ has been to enable rapid development of novel research in electronic structure theory without sacrificing performance on modern parallel computing architectures. With the exception of a few external dependencies, ChronusQ is a standalone software infrastructure completely written in modern C++. The current release of ChronusQ relies on the C++14 standard, while a number of the development streams utilize features outlined in C++17. To this end, extensive use of modern C++ paradigms (SFINAE, polymorphism, etc.) and template metaprogramming are leveraged throughout the code base to enable a level of abstraction which allows developers to write expressive and efficient code. For an examination of some of the more salient aspects of the C++ design of ChronusQ, we refer the reader to the Appendix. ChronusQ utilizes a hybrid parallelism scheme to improve scalability on large computing clusters which leverages both message passing and shared memory protocols to achieve inter- and intranode concurrency, respectively. Calculations involving thousands of CPU cores and thousands of basis functions are regularly performed with ChronusQ on some of the world’s largest

supercomputers [26, 27]. ChronusQ is compatible with any MPI-2 compliant message passing implementation, such as MPICH, OpenMPI and Intel(R) MPI. To allow for the use of ChronusQ on work stations which may not possess an MPI implementation, message passing parallelism is an optional feature which may be enabled or disabled by the build system. Shared memory parallelism is achieved through a combination of the explicit use of OpenMP threads and reliance on threaded external libraries such as those which implement the BLAS [28–31] and LAPACK [32] standards for numerical linear algebra.

After several years of development, ChronusQ has become a full-fledged, standalone, *ab initio* quantum chemistry software package which has proven itself useful both as a development platform to rapidly prototype electronic structure methods, as well as a robust production code capable of tackling complex science problems [18, 26, 33–35]. In this article, we briefly review the design, features and current developments of the ChronusQ software package.

DESIGN AND NOVEL STRUCTURAL FEATURES

Input Specification

ChronusQ utilizes the INI format for the specification of its input. An example ChronusQ input file specification for the time propagation of a single water molecule at the cc-pVTZ / X2C-B3LYP [36, 37] level of theory in the presence of an electric dipole field may be found in Fig. 1. ChronusQ packages a representative subset of commonly used CGTO basis sets, including the Sapporo [38, 39] basis sets commonly used in relativistic calculations, with its source code. Arbitrary CGTO basis sets may be utilized by specifying the full path for the desired basis set file in the Gaussian94 file format. For a detailed examination of the anatomy and options supported by the ChronusQ input file, we refer the reader to the ChronusQ user manual which may be found at <http://www.chronusquantum.org>.

```
[Molecule] # Molecule Specification
charge = 0
mult = 1
geom:
  O      0.000000000  -0.0757918435  0.000000000
  H      0.866811829   0.6014357793  0.000000000
  H     -0.866811829   0.6014357793  0.000000000
[QM] # Job Specification
reference = X2CB3LYP
job = RT
[BASIS] # Basis Set Specification
basis = cc-pVTZ
[RT] # Time-Propagation Parameters
TMAX = 1.0
DELTAT = 0.05
FIELD:
  StepField(0.00, 0.10) Electric 0.000 0.001 0.000
  StepField(0.05, 0.80) Electric 0.008 0.000 0.000
```

Figure 1: An example specification for a RT ChronusQ job. The field specified will add a y electric dipole operator of strength 0.001 AU on $t \in [0, 0.1)$, and a x electric dipole operator of strength 0.008 AU on $t \in [0.05, 0.8)$.

Software Dependencies

While ChronusQ is best described as a *standalone* quantum chemistry software suite, this description is primarily limited to the electronic structure capabilities of the software. ChronusQ relies on a number of external libraries to provide complementary functionality which facilitate efficient implementations of quantum mechanical methods. Where possible and practical, these software dependencies are packaged with the source code itself; however a number of these dependencies must be installed separately and discovered by the build system upon configuration. A list and description of these dependencies is outlined in the ChronusQ user manual.

To ensure portability on many different software configurations across different architectures, ChronusQ utilizes a CMake build system. The CMake build system attempts to determine the existence and linkage of the various dependencies as well as provide specifications of various build options which influence the performance and configuration of ChronusQ such as debug and optimization flags, enabling MPI bindings, etc. A comprehensive guide to the CMake build system may be found in the ChronusQ user manual.

ChronusQ relies extensively on optimized and threaded implementations of BLAS and LAPACK numerical linear algebra standards to ensure high-levels of performance on modern computing architectures. The open source OpenBLAS [40,41] library is packaged with ChronusQ to ensure that such performance is portable to a large number of different architectures. ChronusQ is also compatible with vendor tuned linear algebra software such as the Intel(R) Math Kernel Library (MKL) and IBM Engineering and Scientific Software Library (ESSL) for specific architectures. If MPI has been enabled, ChronusQ may be optionally configured to utilize the ScaLAPACK [42] library to perform high-performance distributed memory linear algebra suitable for large computing clusters.

With the exception of those integrals which are specific to the X2C and GIAO methods implemented in ChronusQ, molecular integrals over contracted Gaussian basis functions are evaluated using the Libint library [43]. ChronusQ was one of the early adopters of the modern C++ interface of the Libint library which has enabled the development of expressive and reusable integral drivers. For the evaluation of exchange-correlation (XC) functionals (and their derivatives) in the KS implementation, ChronusQ utilizes the Libxc library [44,45]. To ensure portability of standardization of the ChronusQ checkpoint and binary files, we utilize the HDF5 library.

General Infrastructure for the Unified Treatment of Electronic Spin

Perhaps the most common motif in the design of ChronusQ is in the general manner with which it treats electronic spin throughout the code base. It is in this context that the development of ChronusQ has benefited from the era in which it has been written: spin was considered a priority from the beginning. Traditionally, quantum chemistry codes are generally written from a “bottom-up” approach as it relates to the breaking of spin symmetries: spin restricted methods (RS: S^2 and S_z eigenfunctions) are written before spin unrestricted (US: S_z eigenfunctions) methods which are written before generalized spin methods (GS: broken spin-symmetry), if such GS treatments are implemented at all. If GS is to be neglected in a particular implementation, this “bottom-up” approach is logical as the Roothaan-Hall equations separate into distinct (but coupled) eigenvalue problems in the binary spin ba-

sis [46],

$$\text{RS / US: } F^\sigma(P^\alpha, P^\beta)C^\sigma = SC^\sigma E^\sigma, \quad \sigma \in \{\alpha, \beta\}. \quad (1)$$

Here α and β are spin indices, S is the basis overlap matrix, and F^σ , C^σ , P^σ , and E^σ are the spin dependent Fock matrix, molecular orbital matrix, density matrix, and diagonal matrix of canonical orbital eigenenergies, respectively. Round brackets, (\cdot) , indicate a functional dependence. However, GS takes the form of a single eigenvalue problem of twice the dimension [47],

$$\text{GS: } F^{2C}(P^{2C})C^{2C} = SC^{2C}E^{2C}, \quad (2)$$

where

$$X^{2C} = \begin{bmatrix} X^{\alpha\alpha} & X^{\alpha\beta} \\ X^{\beta\alpha} & X^{\beta\beta} \end{bmatrix}, \quad X \in \{F, P\}. \quad (3)$$

Generalizing a code base from RS to US requires the manipulation of one additional density/Fock matrix whereas generalization of US to GS requires the manipulation of one fewer density/Fock matrix. GS almost seems artificial in this treatment as it more closely resembles RS in the context of the manipulation of individual matrices but resembles US in the treatment of multiple spin degrees of freedom. Such a structure requires a significant amount of logic in the code base to control the proper workflow and specialization of many aspects of the code to either work with RS/US or GS. In ChronusQ, the treatment of spin was a primary consideration from the initial development, thus some time was spent in developing a unified code infrastructure that treats RS, US, and GS on an equal footing. To this end, we adopt a “top-down” approach to spin manipulation such that GS is a generalization of US which is a generalization of RS, as would be implied by the successive restriction of the wave function to be an eigenfunction of S_z and S^2 . Such a structure is possible through a change of spin basis to the Pauli spin basis [27, 48],

$$X^{2C} = \sum_{I=0}^3 X^I \otimes \sigma_I, \quad (4)$$

where

$$2X^0 = X^{\alpha\alpha} + X^{\beta\beta}, \quad (5a)$$

$$2X^1 = X^{\alpha\beta} + X^{\beta\alpha}, \quad (5b)$$

$$-2iX^2 = X^{\alpha\beta} - X^{\beta\alpha}, \quad (5c)$$

$$2X^3 = X^{\alpha\alpha} - X^{\beta\beta}, \quad (5d)$$

and $\{\sigma_I\}$ is the set of Pauli matrices with σ_0 representing the 2x2 identity matrix. X^0 is referred to as the scalar component of the spinor operator X^{2C} , while X^1 , X^2 and X^3 are referred to as its spin components. In this basis, specialization from GS to US to RS simply implies the removal of certain spin components of density and Fock matrices. Thus, in ChronusQ, spin-dependent operators are stored internally as collections of scalar and spin components according to

$$F = \begin{cases} F^0 \otimes \sigma_0 + F^1 \otimes \sigma_1 + F^2 \otimes \sigma_2 + F^3 \otimes \sigma_3 & \text{GS} \\ F^0 \otimes \sigma_0 + F^3 \otimes \sigma_3 & \text{US} \\ F^0 \otimes \sigma_0 & \text{RS} \end{cases} \quad (6)$$

The use of this scheme for spin separation is primarily a mechanism to enable a readable and expressive code structure void of fringe logic to handle the manipulation of the different spin cases. Internally, the eigenvalue problems solved for the Roothaan-Hall equations are exactly those given in Eqs. (1) and (2). In the case of the molecular orbital matrix and canonical orbital eigenvalues, no such simplification can be made. However, due to the fact that ChronusQ is primarily a single-reference quantum chemistry code, the majority of the functionality may be implemented through the use of the density matrix as opposed to the orbitals directly. Thus the vast majority of the code base benefits from this spin separation scheme. The manipulation of the cases for the eigenvalue problem is facilitated through templated matrix utilities which efficiently convert between the two formats, which yields only minimal effect on the overall structure of the code base. In practice, we have found the following points to be the primary motivation for the chosen approach for the treatment of spin in ChronusQ:

1. Generalization of a method to support two-component spinors is systematic. If a method may be expressed in the Pauli spin basis, generalization is typically as simple as performing some set of mathematical operations on the scalar component followed by another set of (possibly different) operations on the spin components (e.g. Eq. (8))
2. The off-diagonal matrices $X^{\alpha\beta}$ and $X^{\beta\alpha}$ are generally non-Hermitian, while X^2 and X^3 are Hermitian as long as X^{2C} is Hermitian. Thus when constructing moieties such as $K(X^i)$ (see Eq. (8)), the symmetry of X^i may be utilized; reducing the number of floating point operations in direct contraction schemes.
3. The manipulation of general (possibly spin dependent) perturbations as they relate to the Hamiltonian and the evaluation of molecular properties is straight forward. All perturbations which are spin independent (such as electric multipoles, electron-nuclear interaction, etc.) only appear in the scalar Fock matrix, while those which are spin dependent (such as magnetic fields) only appear in the spin components of the Fock matrix. Further, due to the fact that the Pauli matrices are traceless, the expectation value of a general one particle spinor operator, O^{2C} , with respect to the one particle spinor density matrix, P^{2C} , may be expressed as [27, 48]

$$\langle O^{2C} \rangle = \text{Tr} [O^{2C} P^{2C}] = 2 \sum_{I=0}^3 \text{Tr} [O^I P^I] \quad (7)$$

CURRENT PROGRAM FEATURES

Ground State Methods

Reference Wave Functions

ChronusQ implements a general self-consistent field (SCF) module which provides a unified treatment of RS, US, and GS spin symmetries to obtain ground state wave functions described by either Hartree-Fock (HF) or Kohn-Sham density functional theory (KS) approximations. Within the general framework for the treatment of spin described in the

previous section, the HF Fock matrix may be expressed as [27, 48]

$$F^0 = h^0 + J(P^0) - K(P^0), \tag{8a}$$

$$F^k = h^k - K(P^k), \quad k \in \{1, 2, 3\}, \tag{8b}$$

where h is the core Hamiltonian, and J and K are the Coulomb and exchange matrices, respectively. Thus the treatment of RHF, UHF and GHF may be expressed simply by forming additional exchange terms for the required spin components of the density matrix. The formation of the Fock matrix is based on the direct SCF scheme of Almlöf, *et al.* [49] using a integral screening scheme resembling that of the LinK method [50].

The formation of the KS Fock matrix in ChronusQ adopts a form analogous to Eqs. (6) and (8) for the RKS, UKS and GKS methods [27, 48]. For the use of two-component spinor density, ChronusQ utilizes a set of torque free auxiliary variables which allow the adaptation of collinear XC functionals for use with non-collinear densities [27, 51]. This non-collinear DFT formalism preserves the self-consistent, global zero-torque theorem for the XC magnetic field [52] while admitting the ability to yield non-zero local torque. In practice, it is the local torque which allows for the accurate description of spin dynamics and time-evolution of the spin density [52–57]. The XC integration and batching scheme adopted in ChronusQ closely resembles that of Stratmann, *et al.* [58]. The assembly of the XC potential in ChronusQ generalizes the scheme of Burow, *et al.* [59] for use with open-shell and spinor densities [27]. ChronusQ supports local density (LDA), generalized gradient (GGA), and hybrid approximations for the XC functional. The formation of both the HF and KS Fock matrix is efficiently parallelized using both inter- and intranode communication schemes. Ref 27 demonstrates the linear scaling (strong and weak) of the KS implementation in ChronusQ.

Relativistic Effects and External Magnetic Fields

Relativistic effects may be included variationally in the SCF procedure for both HF and KS wave functions through the exact two-component (X2C) method [6–11]. Practically, the extension of the SCF module to implement the X2C-HF and X2C-KS methods simply amounts to the manipulation of additional spin components for the core Hamiltonian in Eq. (8). To ensure numerical stability, relativistic calculations are performed using Gaussian

charge models [60] for nuclear charge distributions rather than the point charge distributions typically used in non-relativistic theory. For calculations including one-electron spin orbit contributions to the core Hamiltonian, Boettger scaling [61] is used to approximately account for the higher-order two-electron terms. ChronusQ also supports SCF optimization in the presence of finite magnetic fields through the use of gauge including atomic orbitals (GIAO) [12, 13] at the GIAO-RHF [15], GIAO-UHF, and GIAO-GHF levels of theory [17, 18]. For the formation of the GIAO Fock matrix, the magnetic field manifests both as explicit terms added to the spin component of the Fock matrix as well as an implicit dependence of the CGTO basis function through the addition of a complex phase factor,

$$\chi^{\text{CGTO}}(\mathbf{r} - \mathbf{R}) \mapsto \exp\left(\frac{i}{2}(\mathbf{R} \times \mathbf{B}) \cdot (\mathbf{r} - \mathbf{R})\right) \chi^{\text{CGTO}}(\mathbf{r} - \mathbf{R}), \quad (9)$$

where χ^{CGTO} is a CGTO centered at \mathbf{R} and \mathbf{B} is the external magnetic field. In addition, ChronusQ includes orbital–Zeeman, spin–Zeeman, and diamagnetic field interactions of the non-relativistic Pauli Hamiltonian in the GIAO methods [14, 15, 17, 18]. GIAO Fock matrices may be formed directly in the AO basis through a generalization of the direct SCF method of Almlöf, *et al.* [49] for complex integrals. To the best of the authors’ knowledge, ChronusQ contains the only publicly available implementation of two-component spinor GIAO methods [18] at this time.

Self-Consistent Field Optimization

ChronusQ implements both first and second order optimization schemes for the ground state SCF wave function. First order SCF optimization utilizes the widely adopted [62–65] scheme involving a combination of damping and direct inversion in the iterative subspace (DIIS) extrapolation of the Fock and density matrices to accelerate convergence. Second order optimization may proceed by either the quadratically convergent SCF method of Bacskey [66], the stability check and perturbation method [67, 68], or some combination of the two. Typically, the best results for the optimization of GSCF wave functions in ChronusQ involves first order optimization of the wave function to a stationary saddle point followed by second order optimization to the minimum energy solution. For a full description of the SCF control options supported by ChronusQ, we refer the reader to the ChronusQ user manual.

Real-Time Electronic Dynamics

One of the hallmarks of the functionality contained in ChronusQ is the implementation of real-time propagation for quantum systems in the presence of external perturbations, as well as its general implementation of such functionality with respect to the treatment of electronic spin. Real-time propagation is important in the study of matter-field interaction due to the fact that it is non-perturbative relative to the strength of the external perturbation; both linear and non-linear effects may be captured through proper analysis [69–73]. This class of real-time functionality is encapsulated in the RT module of ChronusQ. For a complete description of the specification of options for the RT module in ChronusQ, we refer the reader to the ChronusQ user manual.

Fundamentally, the RT module solves the non-linear Liouville-von Neumann equation [74, 75],

$$i\hbar\partial_t P(t) = [F(P(t), t), P(t)]. \quad (10)$$

Formally, Eq. (10) may be solved (propagated) exactly in the time domain through the Magnus expansion of the time-domain propagator [76],

$$P(t) = U(t, t_0)P(t_0)U(t, t_0)^\dagger, \quad U(t, t_0) = \exp(\Omega(t, t_0)), \quad (11)$$

where $\Omega(t, t_0)$ is a non-terminating series expansion which must be truncated in practice. Many explicit and implicit time integration methods may be derived from the Magnus expansion of the propagator [72, 77, 78] of which ChronusQ implements a functional subset. The default integration scheme in ChronusQ is the modified midpoint unitary transformation (MMUT) method of Li, *et al.* [79]. MMUT is a symplectic multi-step (leap-frog), explicit integration scheme based on the Magnus expansion with error formally $\mathcal{O}(\Delta t^2)$,

$$P(t_{k+1}) = U_{\text{MMUT}}(t_k)P(t_{k-1})U_{\text{MMUT}}^\dagger(t_k), \quad U_{\text{MMUT}}(t_k) = \exp\left(-\frac{2i\Delta t}{\hbar}F(P(t_k), t_k)\right). \quad (12)$$

The leap-frog character of MMUT exhibits an excellent trade off between accuracy and efficiency over other Magnus-based expansions for the oscillatory solutions which are characteristic of these types of simulations. Because MMUT is a leap-frog method, a non-leap-frog step must be used to seed and restart the integration every so often to maintain accuracy and

stave off energy drift [79]. For this purpose, the default seed and restart step in ChronusQ is the explicit second order (trapezoidal) Magnus (EM2) propagator given by [78]

$$P(t_{k+1}) = U_{\text{EM2}}(t_k)P(t_k)U_{\text{EM2}}^\dagger(t_k), \quad U_{\text{EM2}}(t_k) = \exp\left(-\frac{i\Delta t}{\hbar}F_m(t_k, t_{k+1})\right), \quad (13)$$

where

$$F_m(t_k, t_{k+1}) = \frac{1}{2}(F(P(t_k), t_k) + F(P_{\text{FE}}(t_{k+1}), t_{k+1})), \quad (14)$$

$$P_{\text{FE}}(t_{k+1}) = U_{\text{FE}}(t_k)P(t_k)U_{\text{FE}}^\dagger(t_k), \quad U_{\text{FE}}(t_k) = \exp\left(-\frac{i\Delta t}{\hbar}F(P(t_k), t_k)\right). \quad (15)$$

For both the MMUT and EM2 integration methods, the matrix exponential may be formed using either exact diagonalization based methods, or approximate Taylor series and Chebyshev series expansions [77, 80, 81]. The latter approximate approaches yield drastic performance improvements for large quantum systems/basis sets due to the poor scaling and parallelization of eigenvalue decomposition.

ChronusQ admits the ability to express an arbitrary number of (one-body) time-dependent external perturbations, $\{V_\xi(t)\}$, of the form

$$F(P(t), t) = F_0(P(t)) + \sum_{\xi}^{N_{\text{pert}}} V_\xi(t), \quad (16)$$

where F_0 is only implicitly time-dependent through the time dependence of the density matrix. Generally, a particular perturbation takes the functional form

$$V_\xi(t) = V_\xi \cdot f(t)(\Theta(t - t_{\text{on}}) - \Theta(t - t_{\text{off}})), \quad (17)$$

where Θ is the Heaviside step function, $t_{\text{on/off}}$ are reference times to turn the perturbation on and off, V_ξ is a physical, time-independent one-body operator, and $f(t)$ is an envelope function which describes the time dependence and amplitude of the perturbation. For V_ξ , ChronusQ supports both the length and velocity gauge electric multipole operators up through the electric octupole, and the magnetic dipole operator. Additionally, ChronusQ

supports the following envelope functions:

$$f(t) = \kappa \cdot \begin{cases} 1 & \text{Step Function} \\ t - t_{\text{on}} & \text{Linear Ramp} \\ \cos(\omega(t - t_{\text{on}})) & \text{Plane Wave} \\ \exp(-\alpha(t - t_{\text{on}})^2) & \text{Gaussian} \end{cases}$$

where κ is a chosen parameter to control the amplitude of the perturbation. An example field specification is given in Fig. 1.

Throughout the time-propagation, ChronusQ evaluates the time-dependent expectation values of various one body operators, $\{O_\zeta\}$, according to

$$\langle O_\zeta(t) \rangle = \text{Tr} [O_\zeta P(t)]. \quad (18)$$

Depending on the spin characteristics of O_ζ , Eq. (18) may be efficiently evaluated according to Eq. (7). For example, evaluation of a time-dependent component (i.e. the z component) of the electric dipole amounts to only evaluating the trace of the z -dipole matrix with respect to the scalar density matrix, while evaluating a component of the (z) component of the magnetic dipole requires evaluating the trace of the z -magnetic dipole with respect to $P^3(t)$. The supported choices for O_ζ are the same as those for V_ξ outlined above. The time-series for the desired time-dependent expectation values may be obtained from the ChronusQ checkpoint file after the calculation for post processing at the users' discretion. Using these time-series, users may simulate quantities such as absorption spectra [72, 82], electric and magnetic circular dichroism spectra [35, 83], charge transfer [84–86], and second harmonic generation [71, 87].

Frequency Domain Methods

In addition to time-domain methods, ChronusQ implements a suite of frequency domain methods to solve time-dependent problems in the RESP module. For a full description of the RESP module and its input specification, we refer the reader to the ChronusQ user manual. As opposed to explicit, non-perturbative solution of Eq. (10) in the time domain,

these methods solve Eq. (10) in the frequency domain under a series of approximations, namely that the applied perturbation is weak in field strength and harmonic in the time domain. Under these approximations, solution of Eq. (10) (or more specifically Eq. (18)) instead becomes a large linear algebra problem to obtain the quantum propagator in the frequency domain. Frequency domain methods fall into one of two classes: residue methods and response methods. In this section, we review the salient aspects of the implementation of these methods in ChronusQ.

Residue Methods

The quantum propagator diverges in the frequency domain at frequencies which correspond to transition energies of the quantum system [19]. Residue methods aim to determine the poles and residues of the propagator at these frequencies, thus obtaining information pertaining to the excited states of the quantum system such as transition energies and densities. For the single determinant reference wave functions implemented in ChronusQ, residue methods generally take the form of a large generalized eigenvalue problem of a matrix pencil (H, S) ,

$$HT = ST\Omega, \tag{19}$$

where the form of H and S are dependent on the representation of the reference wave function (i.e. in the case of HF/KS response, H represents the orbital Hessian and S is an indefinite metric [19–21]). In general, the columns of the eigenvectors T represent the transition density pertaining to the transition energies of the corresponding diagonal element of Ω . ChronusQ supports residue calculations using two different approximations of the quantum propagator, namely particle-hole (ph-RPA) [19–21] and particle-particle (pp-RPA) [22–24] random phase approximations. Both HF or KS reference wave functions may be used for either of these propagator approximations. Determining propagator poles and residues under the ph-RPA yields information relating to neutral (particle number conserving) excitations of the quantum system in question, while those corresponding to the pp-RPA yield information pertaining to two electron addition (double electron affinity) and removal (double ionization). Additionally, ChronusQ supports inclusion of both relativistic effects (the X2C-ph-RPA [88] and X2C-pp-RPA [89] methods) and magnetic fields (the GIAO-ph-RPA method [33, 90])

in its residue calculations. The GIAO-ph-RPA method using GIAO-RHF and GIAO-GHF reference wave functions have enabled the calculation of linear response approximations for the magnetic circular dichroism spectra of closed shell systems [33]. To the best of the authors’ knowledge, ChronusQ contains the only publicly available implementation of the GIAO-ph-RPA method at this time. We note for clarity that the GIAO-ph-RPA method, as implemented in ChronusQ, treats the linear response of molecular systems to external perturbations in the presence of explicit finite, static magnetic fields. We are careful to make this distinction in this work to avoid confusion with work on perturbative GIAO response methods such as those developed by Kjærgaard, *et al* [91,92].

Generally, the dimension of H is too large to directly diagonalize using methods such as those provided in (Sca)LAPACK. For these large problems, ChronusQ implements the iterative generalized preconditioned locally harmonic residual (GPLHR) method [93,94] to perform the diagonalization. Rather than obtaining all possible eigenvalues of (H, S) , the GPLHR method performs a partial diagonalization for a select number of desired eigenvalues. Unlike the more typically utilized Davidson (Lanczos) method [95–97], GPLHR is able to directly (and robustly) solve for eigenpairs in the spectral interior of (H, S) , thus making it an ideal solver for high-energy spectroscopies such as X-Ray absorption [98]. Like the Davidson method, GPLHR only requires the specification of action (product) of (H, S) onto a trial set of vectors to perform the diagonalization. ChronusQ implements direct, density based contraction schemes to perform the matrix products for both the ph-RPA [99] and pp-RPA [24] methods. Because transition densities exhibit the same spin factorization as the density matrix (Eq. (4)) [88], the direct contractions closely resemble those of Eq. (8) in the AO basis, only with a non-Hermitian density operator. As such, the generalization of the residue calculations to use RS, US and GS reference wave functions closely resembles the structure of the Fock matrix formation.

Linear Response Methods

Evaluation of the residues may be avoided entirely if the moiety of interest is Eq. (18) in the frequency domain. Within the linear response (weak perturbation) approximation, frequency dependent properties may be evaluated directly through the solution of a shifted system of

linear equations given by [100–102]

$$\langle O_\zeta \rangle = \langle \langle O_\zeta; V_\xi \rangle \rangle_\omega^\gamma \approx \mathbf{O}_\zeta^\dagger \mathbf{X}_\xi(\omega), \quad (20a)$$

$$(H - (\omega + i\gamma)S)\mathbf{X}_\xi(\omega) = \mathbf{V}_\xi. \quad (20b)$$

Here, O_ζ and V_ξ are defined as they were in Eqs. (16) and (18), respectively, and (H, S) is the same pencil as Eq. (19). γ is a complex damping parameter which ensures convergence of the propagator at all frequencies (including poles) [101]. The boldface \mathbf{O}_ζ and \mathbf{V}_ξ are property gradients defined by the selection of the propagator approximation and operators O_ζ and V_ξ , respectively [19]. ChronusQ currently supports linear response calculations using the ph-RPA only. Much like the residue methods, the dimension of H is often too large to factorize or invert directly using (Sca)LAPACK. As such, ChronusQ provides an implementation of the generalized minimum residual (GMRES) method [103] to iteratively solve large linear systems of the form of Eq. (20b).

In addition to providing solvers which solve Eq. (20b) in the full dimension of H , ChronusQ implements a series of model order reduction (MOR) techniques [26, 104] to improve the efficiency of evaluating Eq. (20b) for multiple frequencies in a spectral region of interest. The MOR technique constructs a rational Krylov subspace which interpolates Eq. (20a) in the frequency domain. The subspace is constructed as the linear span of solutions to Eq. (20b) at multiple, carefully chosen interpolation frequencies. Using Galerkin projection under the constructed subspace, the full dimensional problem is projected onto a reduced space problem which is rapidly evaluatable. The MOR method implemented in ChronusQ has been demonstrated to provide excellent approximations to the X-Ray absorption spectrum for large molecular systems with quadratic computational scaling. ChronusQ was the first software to provide such MOR functionality and remains the sole publicly available implementation at this time to the best of the authors’ knowledge.

CURRENT DEVELOPMENTS

As is the case with many research codes, there are a number of development streams which have not yet made it into the primary release of ChronusQ. In this section, we examine

some of the most recent development in the ChronusQ ecosystem which will be folded into forthcoming releases.

Kohn–Sham Density Functional Theory in Magnetic Fields

Magnetic density functional theory (BDFT) strikes a balance between cost and accuracy for simulating molecules in magnetic fields [105]. Currently, the released version of ChronusQ only supports GIAO basis functions for the treatment of finite magnetic fields within the GIAO-HF level of theory. GIAO-RKS reference wave functions [106–108] are currently supported in the development version of ChronusQ, and will be present in the forthcoming release.

Quantum Embedding Methods

In recent years, quantum embedding capabilities have been developed in ChronusQ [34]. Currently, users may perform an embedded SCF calculation by specifying both an embedding potential and embedding magnetic field on a real space grid using the XSF file format [109]. Such moieties have regularly been obtained using a combination of the Abinit [110] software and the software presented in previous work by Huang, *et al.* on embedding [111]. CGTO basis representations of the embedding perturbations are produced by numerical integration of the interpolated real space representations using a similar scheme as the one used for the XC integration for KS methods in ChronusQ (for details, see [34]). Embedded SCF calculations are supported for RSCF, USCF, and GSCF optimizations for both HF and KS levels of theory. Embedding X2C-HF/KS wave functions is currently under development.

Two-Component Post-SCF Methods

The development version of ChronusQ includes working implementations of both ground- and excited-state post-SCF methods. Among the ground-state post-SCF methods, standard second-order Møller-Plesset perturbation theory (MP2) [112], approximate second-order coupled-cluster (CC2) [113], and coupled-cluster with single and double excitations (CCSD) [25] have been implemented. For post-SCF excited states, ChronusQ includes

an implementation of the time-dependent (TD) equation-of-motion coupled-cluster (EOM-CC) [114–116] formalism of Nascimento and DePrince [117, 118], in both the TD-EOM-CC2 and TD-EOM-CCSD flavors.

Unlike other reported time-dependent coupled-cluster implementations [119–123], the TD-EOM-CC formalism in ChronusQ is based on the time evolution of a coupled-cluster dipole moment function from which one can obtain a spectral line shape function, $I_\xi(\omega)$, defined as

$$I_\xi(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \Phi_0 | (\hat{1} + \hat{\Lambda}) \bar{\mu}_\xi e^{i\bar{H}_N t} \bar{\mu}_\xi | \Phi_0 \rangle, \quad \xi \in \{x, y, z\}. \quad (21a)$$

Here, $\bar{\mu}_\xi$ represents the ξ -component of the similarity-transformed electric dipole operator

$$\bar{\mu}_\xi = e^{-\hat{T}} \hat{\mu}_\xi e^{\hat{T}} \quad (22)$$

and \bar{H}_N represents the normal-ordered similarity-transformed Hamiltonian

$$\bar{H}_N = e^{-\hat{T}} \hat{H} e^{\hat{T}} - E_{CC}. \quad (23)$$

The symbols E_{CC} , \hat{T} , and $\hat{\Lambda}$ represent the energy, excitation operator, and de-excitation operator associated with the ground-state CC wavefunction, respectively. The real part of the line shape function defines oscillator strengths

$$f(\omega) = \frac{2}{3} \omega \sum_{\xi} \Re\{I_\xi(\omega)\}. \quad (24)$$

which may be evaluated over an arbitrarily broad energy window [117, 118].

A notable feature of the ground- and excited-state implementations discussed here is that they rely on the same template metaprogramming techniques employed throughout the rest of ChronusQ (see Appendix) and thus are compatible with both real and complex RHF, UHF, and GHF (including X2C-HF) reference wavefunctions. Hence, like many other reported implementations of time-independent relativistic EOM-CC theory [124–138], the X2C-based TD-EOM-CC2 and TD-EOM-CCSD algorithms in ChronusQ incorporate spin-orbit and scalar relativistic effects from first principles. To the best of the authors' knowledge, this implementation is the only one that incorporates spin-orbit coupling within a time-dependent EOM-CC formalism at this time. Active effort is also being undertaken toward the development of standard (frequency domain) EOM-CC methods [116] within ChronusQ.

CONCLUSIONS

ChronusQ is a standalone, high-performance quantum chemistry software package specializing in time-dependent and relativistic electronic structure methods. Special emphasis is placed on the general treatment of electronic spin throughout the code base, allowing for the implementation of electronic structure methods with various spin symmetries while requiring only minor code modifications. Further, the modern C++ code design adopted by ChronusQ allows for the expression of complex quantum chemistry algorithms in a readable, generic, and elegant manner. Thus, as a development code, ChronusQ has proven to be a near optimal platform for the rapid development of novel electronic structure methods. In addition, with extensive exploitation of high performance numerical linear algebra software, and use of both shared and message passing parallelism schemes, ChronusQ is a performant, production quality quantum chemistry code which is suitable for both workstations and supercomputers alike.

In this article, we reviewed much of the salient aspects of the functionality implemented in the ChronusQ program as well as a number of the current developments which will accompany its upcoming release. The core of the functionality in ChronusQ revolves around the solution of time-dependent electronic structure problems in either the time or frequency domain. ChronusQ supports the inclusion of relativistic effects in the electronic wave function through the X2C method throughout the code. This support is enabled in part by the general manner with which ChronusQ treats electronic spin, as outlined in the main text. Further, ChronusQ supports the inclusion of finite, uniform magnetic fields as external perturbations in all HF based electronic structure methods. Implementations of methods such as GIAO-GHF and the GIAO-ph-RPA in ChronusQ are, at the time this article has been written and to the best of the authors' knowledge, the sole implementations of these methods in publicly available, open source quantum chemistry codes. Further, ChronusQ provides implementations of cutting edge numerical linear algebra algorithms such as the GPLHR method, and MOR approximations for problems arising in linear response theory. To the best of the authors' knowledge, ChronusQ provides the sole implementation of MOR functionality for linear response problems available to the public.

ChronusQ is a *free* (as in *software freedom*) quantum chemistry software package which is open to the public. Contributions from the quantum chemistry community as a whole are not only allowed, but encouraged. ChronusQ may be obtained online through our website <http://www.chronusquantum.org>. This website also contains the ChronusQ Wiki and user manual which serve as the most up-to-date references for the functionality contained in ChronusQ.

ACKNOWLEDGMENTS

The development of Chronus Quantum ChronusQ computational software is supported by the National Science Foundation (OAC-1663636 to X.L. and A.E.D.). The method development of magneto-optical spectroscopy is supported by National Science Foundation (CHE-1856210 to X.L.), and the development of relativistic electronic structure theory is supported by the Office of Science, US Department of Energy ([de-sc0006863](#) to X.L.). E.V. was partially supported by the U.S. National Science Foundation (award 1550456).

AUTHOR CONTRIBUTIONS

The overall structure and modern C++ design of ChronusQ is due to David B. Williams-Young (DBWY). Parallelism in ChronusQ is also due to DBWY. The name “Chronus Quantum” is due to Joshua J. Goings (JJG). The development of memory management utilities in ChronusQ is due to DBWY, Torin F. Stetina (TFS), and Andrew Wildman (AW). The development of the ground state SCF module is due to DBWY, Patrick Lestrangle (PL), TFS, and Xiaosong Li (XL). The development of DFT related methods is due to Alessio Petrone (AP), DBWY and TFS. ChronusQ primarily utilizes the Libint library to evaluate molecular integrals over contracted Gaussian basis functions. The Libint library is due to Edward F. Valeev (EFV), and its integration into ChronusQ is due to DBWY and EFV. ChronusQ also contains an in house integral code which performs molecular integral evaluations for those integrals which are not provided by Libint, such as those required by the GIAO and X2C methods. The in house integral code is due to Shichao Sun (SS) and XL.

The development of GIAO capabilities in ChronusQ are due to SS and XL. The development of the X2C method in ChronusQ is due to DBWY and Joseph Kasper.

The RT module is due to DBWY, AP, AW, SS, JJG, and Feizhi Ding. The MMUT algorithm implemented in the RT module is due to XL. The RESP module and the development of the MOR capabilities in ChronusQ are due to DBWY. The extension of DFT and GIAO capabilities to the RESP module are due to AP and SS, respectively. Validation of the RESP module is in large part due to TFS and AW.

The development of embedding methods in ChronusQ is due to Chad E. Hoyer. The development of post-SCF methods such as Coupled Cluster and Møller-Plesset perturbation theory is due to DBWY, Daniel R. Nascimento, Lauren Koulias, and A. Eugene DePrince III. The tensor contractions required by these post-SCF methods are efficiently performed by the TiledArray library, which is due to EFV.

APPENDIX: MODERN C++ SOFTWARE DESIGN

The adoption of modern C++ in ChronusQ has allowed for a level of abstraction throughout the code base which has enabled the development of expressive, reusable and efficient code. ChronusQ was originally written in C++11, but more recently we have adopted a number of features in the C++14 standard (such as generic lambda expressions, variable templates, etc.) to decrease verbosity and improve expressiveness throughout the code. Current development streams of ChronusQ require features from C++17 (such as polymorphic memory resources, template deduction, etc.); however, these features will not be merged into the release stream until the standard is more widely supported in vendor C++ compilers. In this appendix we review a number of the more salient aspects on the modern C++ design of ChronusQ.

Template Metaprogramming

The use of template metaprogramming in ChronusQ is primarily motivated by the fact that we wish to develop code which supports both real and complex wave functions with maximal code reuse and minimal duplication of type-generic implementation details. To this end, the use of templates allows for the specialization of a certain number type-specific

implementation details while allowing the developer to express their algorithms in a type-generic manner.

In electronic structure theory, the majority of the type-specific implementation details are encapsulated in the use of linear algebra software. Such operations include matrix multiplication, diagonalization, etc. Implementations of the BLAS and LAPACK standards are typically expressed in either the C or FORTRAN programming languages such that their calling APIs are type-specific, i.e. the multiplication of two real (double precision) matrices (DGEMM) is performed using a different function than the one that performs the multiplication of two complex (double precision) matrices (ZGEMM). However, the generic structure of these APIs (i.e. the general information one needs to pass to perform the operation such as data pointers, dimensions, etc.) are invariant between the function calls. To this end, ChronusQ implements templated wrappers around a functional subset of the BLAS and LAPACK standards to provide uniform calling API which allows for their integration into type-generic algorithmic structures. In addition, ChronusQ also provides type-generic templated wrappers for the MPI API to a similar effect. We note for completeness that similar functionality is currently being developed and standardized in the BLAS++, LAPACK++, and SLATE software libraries [139]. There are currently development efforts to integrate such software into ChronusQ.

Type Independent API and Dynamic Polymorphism

Due to the fact that ChronusQ supports many combinations of methods throughout the code base (i.e. non-relativistic, time-dependent, X2C, GIAO, etc.), the majority of the core functionality must be templated over both a type which describes the wave function and a type which describes the basis functions to maintain a type-generic development platform. However, because C++ is strongly typed, providing a type-generic API for type-agnostic operations such as performing the self consistent field (SCF) optimization would require the calling program to implement a combinatorial number of paths to perform these operations for every allowable combination of template parameters. To solve this problem in ChronusQ, we have adopted an object oriented code structure which separates type agnostic interfaces from type dependent implementations through the use of dynamic polymorphism.


```

// Type independent API specification
class SingleSlaterBase {
    // Type Independent API
    void SCF(); // calls formFock, etc.
    ...
    // Type Dependent API
    virtual void formFock(...) = 0;
    virtual void contractOrbHess(...) = 0;
    ...
};

// Type-generic SingleSlater implementation
template <typename WfnT, typename IntT>
class SingleSlater : public SingleSlaterBase {
    // Internal storage, etc.
    ...
    // Type specific implementations
    void formFock(...) override { ... };
    void contractOrbHess(...) override { ... };
    ...
};

```

Figure 2: Code snippet which demonstrates the separation of type independent algorithmic specification and type generic implementation for the `SingleSlater` class in ChronusQ. `WfnT` and `IntT` represent the data types describing the electronic wave function and molecular integrals, respectively.

To demonstrate this state of affairs, we examine the code snippet in Fig. 2 which describes the implementation of the `SingleSlater` class in ChronusQ. `SingleSlater` implements the minimum necessary functionality (i.e. formation and storage of the Fock matrix, contractions with the orbital Hessian for response calculations, etc.) for the description of the electronic wave function as a single Slater determinant. In this example, `SingleSlaterBase` provides a type erased API which is accessible from the calling program to perform type agnostic operations. Additionally, `SingleSlaterBase` provides the required API specification for functionality in which the underlying implementation must be type dependent, i.e. Fock matrix formation and storage, etc. These functions are left as pure virtual to ensure that any derived class must provide their implementations. Using the derived implementations of the type dependent operations, one may implement operations such as the SCF optimization in a type agnostic manner.

References

- [1] Li X, Williams-Young D, Valeev EF, Petrone A, Sun S, Stetina T, et al.. Chronus Quantum, Beta 2 Version; 2018. Available from: <http://www.chronusquantum.org>.
- [2] Repisky M, Komorovsky S, Malkin VG, Malkina OL, Kaupp M, Ruud K, with contributions from Bast R, di Remigio R, Ekström U, Kadek M, Knecht S, Konecny L, Malkin E, and Malkin Ondik I. ReSpect 5.1.0 (2019), relativistic spectroscopy DFT program; 2019. Available from: <http://www.respectprogram.org>.
- [3] Saue T, Visscher L, Jensen HJAa, and Bast R, with contributions from Bakken V, Dyall KG, Dubillard S, Ekström U, Eliav E, Enevoldsen T, Faßhauer E, Fleig T, Fossgaard O, Gomes ASP, Hedegård ED, Helgaker T, Henriksson J, Iliaš M, Jacob ChR, Knecht S, Komorovský S, Kullie O, Lærdahl JK, Larsen CV, Lee YS, Nataraj HS, Nayak MK, Norman P, Olejniczak G, Olsen J, Olsen JMH, Park YC, Pedersen JK, Pernpointner M, di Remigio R, Ruud K, Sałek P, Schimmelpfennig B, Shee A, Sikkema J, Thorvaldsen AJ, Thyssen J, van Stralen J, Villaume S, Visser O, Winther T,

- and Yamamoto S. DIRAC, a relativistic ab initio electronic structure program, Release DIRAC18 (2018); 2018. Available from: <http://www.diracprogram.org>.
- [4] Aidas K, Angeli C, Bak KL, Bakken V, Bast R, Boman L, et al. The Dalton quantum chemistry program system. *WIREs Comput Mol Sci*. 2014;4(3):269–284. Available from: <http://doi.org/10.1002/wcms.1172>.
- [5] Shiozaki T. BAGEL: Brilliantly Advanced General Electronic-structure Library. *Wiley Interdisciplinary Reviews: Computational Molecular Science*. 2018;8(1):e1331. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wcms.1331>.
- [6] Kutzelnigg W, Liu W. Quasirelativistic Theory Equivalent to Fully Relativistic Theory. *J Chem Phys*. 2005;123(24):241102. Available from: <https://doi.org/10.1063/1.2137315>.
- [7] Liu W, Peng D. Infinite-Order Quasirelativistic Density Functional Method Based on the Exact Matrix Quasirelativistic Theory. *J Chem Phys*. 2006;125(4):044102. Available from: <https://doi.org/10.1063/1.2222365>.
- [8] Iliáš M, Saue T. An Infinite-Order Two-Component Relativistic Hamiltonian by a Simple One-Step Transformation. *J Chem Phys*. 2007;126(6):064102. Available from: <https://doi.org/10.1063/1.2436882>.
- [9] Peng D, Mikkelsen N, Weigend F, Reiher M. An Efficient Implementation of Two-Component Relativistic Exact-Decoupling Methods for Large Molecules. *J Chem Phys*. 2013;138(18):184105. Available from: <https://doi.org/10.1063/1.4803693>.
- [10] Peng D, Liu W, Xiao Y, Cheng L. Making Four- and Two-Component Relativistic Density Functional Methods Fully Equivalent Based on the Idea of “from Atoms to Molecule”. *J Chem Phys*. 2007;127(10):104106. Available from: <https://doi.org/10.1063/1.2772856>.
- [11] Liu W. Big Picture of Relativistic Molecular Quantum Mechanics. *Natl Sci Rev*. 2016;3(2):204–221. Available from: <https://doi.org/10.1093/nsr/nwv081>.

- [12] London F. Théorie quantique des courants interatomiques dans les combinaisons aromatiques. *J Phys Radium*. 1937;8(10):397–409. Available from: <https://hal.archives-ouvertes.fr/jpa-00233534>.
- [13] Ditchfield R. Molecular Orbital Theory of Magnetic Shielding and Magnetic Susceptibility. *J Chem Phys*. 1972;56(11):5688–5691. Available from: <https://doi.org/10.1063/1.1677088>.
- [14] Helgaker T, Jørgensen P. An Electronic Hamiltonian for Origin Independent Calculations of Magnetic Properties. *J Chem Phys*. 1991;95(4):2595–2601. Available from: <https://doi.org/10.1063/1.460912>.
- [15] Tellgren EI, Soncini A, Helgaker T. Nonperturbative Ab Initio Calculations in Strong Magnetic Fields using London Orbitals. *J Chem Phys*. 2008;129(15):154114. Available from: <https://doi.org/10.1063/1.2996525>.
- [16] Irons TJP, Zemen J, Teale AM. Efficient Calculation of Molecular Integrals over London Atomic Orbitals. *J Chem Theory Comput*. 2017;13(8):3636–3649. PMID: 28692291. Available from: <https://doi.org/10.1021/acs.jctc.7b00540>.
- [17] Sen S, Tellgren EI. Non-Perturbative Calculation of Orbital and Spin Effects in Molecules Subject to Non-Uniform Magnetic Fields. *J Chem Phys*. 2018;148(18):184112. Available from: <https://doi.org/10.1063/1.5029431>.
- [18] Sun S, Williams-Young DB, Stetina TF, Li X. Generalized Hartree-Fock with a Non-perturbative Treatment of Strong Magnetic Fields: Application to Molecular Spin Phase Transitions. *J Chem Theory Comput*. 2018;15(1):348–356. Available from: <https://doi.org/10.1021/acs.jctc.8b01140>.
- [19] Oddershede J, Jørgensen P, Yeager DL. Polarization Propagator Methods in Atomic and Molecular Calculations. *Comp Phys Rep*. 1984;2(2):33–92. Available from: [https://doi.org/10.1016/0167-7977\(84\)90003-0](https://doi.org/10.1016/0167-7977(84)90003-0).
- [20] Casida ME. *Recent Advances in Density Functional Methods:(Part I)*. vol. 1. World Scientific; Singapore; 1995.

- [21] Dreuw A, Head-Gordon M. Single-Reference Ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chem Rev.* 2005;105(11):4009–4037. Available from: <https://doi.org/10.1021/cr0505627>.
- [22] Yang Y, van Aggelen H, Yang W. Double, Rydberg and charge transfer excitations from pairing matrix fluctuation and particle-particle random phase approximation. *J Chem Phys.* 2013;139:224105. Available from: <https://doi.org/10.1063/1.4834875>.
- [23] Peng D, van Aggelen H, Yang Y, Yang W. Linear-response time-dependent density-functional theory with pairing fields. *J Chem Phys.* 2014;140:18A522. Available from: <https://doi.org/10.1063/1.4867540>.
- [24] Yang Y, van Aggelen H, Steinmann SN, Peng D, Yang W. Benchmark tests and spin adaption for the particle-particle random phase approximation. *J Chem Phys.* 2013;139:174110. Available from: <https://doi.org/10.1063/1.4828728>.
- [25] Purvis GD, Bartlett RJ. A full coupledcluster singles and doubles model: The inclusion of disconnected triples. *J Chem Phys.* 1982;76(4):1910–1918. Available from: <https://doi.org/10.1063/1.443164>.
- [26] Van Beeumen R, Williams-Young DB, Kasper JM, Yang C, Ng EG, Li X. Model Order Reduction Algorithm for Estimating the Absorption Spectrum. *J Chem Theory Comput.* 2017;13(10):4950–4961. Available from: <http://dx.doi.org/10.1021/acs.jctc.7b00402>.
- [27] Petrone A, Williams-Young DB, Sun S, Stetina TF, Li X. An Efficient Implementation of Two-Component Relativistic Density Functional Theory with Torque-Free Auxiliary Variables. *Euro Phys J B.* 2018;91(7):169. Available from: <https://doi.org/10.1140/epjb/e2018-90170-1>.
- [28] Lawson CL, Hanson RJ, Kincaid DR, Krogh FT. Basic Linear Algebra Subprograms for FORTRAN Usage. *ACM Trans Math Soft.* 1979;5(3):308–323. Available from: <https://doi.org/10.1145/355841.355847>.

- [29] Dongarra JJ, Du Croz J, Hammarling S, Hanson RJ. Algorithm 656: An Extended Set of Basic Linear Algebra Subprograms: Model Implementation and Test Programs. *ACM Trans Math Soft.* 1988;14(1):18–32. Available from: <https://doi.org/10.1145/42288.42292>.
- [30] Dongarra JJ, Cruz JD, Hammarling S, Duff IS. Algorithm 679: A Set of Level 3 Basic Linear Algebra Subprograms: Model Implementation and Test Programs. *ACM Trans Math Soft.* 1990;16(1):18–28. Available from: <https://doi.org/10.1145/77626.77627>.
- [31] Blackford LS, Demmel J, Dongarra JJ, Duff I, Hammarling S, Henry G, et al. An Updated Set of Basic Linear Algebra Subprograms (BLAS). *ACM Trans Math Soft.* 2002;28(2):135–151. Available from: <https://doi.org/10.1145/567806.567807>.
- [32] Anderson E, Bai Z, Bischof C, Blackford S, Demmel J, Dongarra J, et al. *LAPACK Users' Guide*. 3rd ed. Philadelphia, PA: Society for Industrial and Applied Mathematics; 1999. Available from: <https://doi.org/10.1137/1.9780898719604>.
- [33] Sun S, Williams-Young DB, Li X. An ab Initio Linear Response Method for Computing Magnetic Circular Dichroism Spectra with Nonperturbative Treatment of Magnetic Field. *J Chem Theory Comput.* 2019;15(5):31623169. PMID: 30933558. Available from: <https://doi.org/10.1021/acs.jctc.9b00095>.
- [34] Hoyer CE, Williams-Young DB, Huang C, Li X. Embedding Non-Collinear Two-Component Electronic Structure in a Collinear Quantum Environment. *J Chem Phys.* 2019;150(17):174114. Available from: <https://doi.org/10.1063/1.5092628>.
- [35] Stetina TF, Sun S, Williams-Young DB, Li X. Modeling Magneto-Photoabsorption Using Time-Dependent Complex Generalized Hartree-Fock. *ChemPhotoChem.* 2019;p. Accepted. Available from: <https://doi.org/10.1002/cptc.201900161>.
- [36] Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Func-

- tional Force Fields. J Phys Chem. 1994;98(45):11623–11627. Available from: <https://doi.org/10.1021/j100096a001>.
- [37] Dunning TH. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J Chem Phys. 1989;90(2):1007–1023. Available from: <https://doi.org/10.1063/1.456153>.
- [38] Noro T, Sekiya M, Koga T. Correlating basis sets for the H atom and the alkali-metal atoms from Li to Rb. Theor Chem Acc. 2003;109(2):85–90. Available from: <https://doi.org/10.1007/s00214-002-0425-z>.
- [39] Minami T, Matsuoka O. Relativistic Gaussian basis sets for radon through plutonium. Theor Chem Acc. 1995;90(1):27–39. Available from: <https://doi.org/10.1007/BF01119780>.
- [40] Wang Q, Zhang X, Zhang Y, Yi Q. AUGEM: Automatically Generate High Performance Dense Linear Algebra Kernels on x86 CPUs. In: 2013 International Conference for High Performance Computing, Networking, Storage and Analysis (SC). IEEE; 2013. p. 1–12.
- [41] Xianyi Z, Qian W, Yunquan Z. Model-Driven Level 3 BLAS Performance Optimization on Loongson 3A Processor. In: 2012 IEEE 18th International Conference on Parallel and Distributed Systems. IEEE; 2012. p. 684–691.
- [42] Blackford L, Choi J, Cleary A, D’Azevedo E, Demmel J, Dhillon I, et al. ScaLAPACK Users’ Guide. Society for Industrial and Applied Mathematics; 1997. Available from: <https://epubs.siam.org/doi/abs/10.1137/1.9780898719642>.
- [43] Valeev EF. Libint: A library for the evaluation of molecular integrals of many-body operators over Gaussian functions; 2018. Version 2.5.0-beta.1. Available from: <http://libint.valeyev.net/>.
- [44] Marques MAL, Oliveira MJT, Burnus T. LIBXC: A library of exchange and correlation functionals for density functional theory. Com-

- puter Physics Communications. 2012;183(10):2272 – 2281. Available from: <http://www.sciencedirect.com/science/article/pii/S0010465512001750>.
- [45] Lehtola S, Steigemann C, Oliveira MJT, Marques MAL. Recent developments in LIBXC – A comprehensive library of functionals for density functional theory. *SoftwareX*. 2018;7:1 – 5. Available from: <http://www.sciencedirect.com/science/article/pii/S2352711017300602>.
- [46] Szabo A, Ostlund NS. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Courier Corporation; 2012.
- [47] Stuber JL, Paldus J. Symmetry Breaking in the Independent Particle Model. *Fundamental World of Quantum Chemistry: A Tribute Volume to the Memory of Per-Olov Löwdin*. 2003;1:67–139.
- [48] Williams-Young DB. *Towards Efficient and Scalable Electronic Structure Methods for the Treatment of Relativistic Effects and Molecular Response*. The University of Washington; 2018. Available from: <http://hdl.handle.net/1773/42243>.
- [49] Almlöf J, Fægri Jr K, Korsell K. Principles for a direct SCF approach to LICAOMOab-initio calculations. *J Comput Chem*. 1982;3(3):385–399. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/jcc.540030314>.
- [50] Ochsenfeld C, White CA, Head-Gordon M. Linear and sublinear scaling formation of HartreeFock-type exchange matrices. *The Journal of Chemical Physics*. 1998;109(5):1663–1669. Available from: <https://doi.org/10.1063/1.476741>.
- [51] Egidi F, Sun S, Goings JJ, Scalmani G, Frisch MJ, Li X. Two-Component Non-Collinear Time-Dependent Spin Density Functional Theory for Excited State Calculations. *J Chem Theory Comput*. 2017;13(6):2591–2603. Available from: <http://dx.doi.org/10.1021/acs.jpca.7b02905>.
- [52] Capelle K, Vignale G, Györffy BL. Spin Currents and Spin Dynamics in Time-Dependent Density-Functional Theory. *Phys Rev Lett*. 2001 Oct;87:206403. Available from: <https://doi.org/10.1103/PhysRevLett.87.206403>.

- [53] Capelle K, Gyorffy BL. Exploring Dynamical Magnetism with Time-Dependent Density-Functional Theory: From Spin Fluctuations to Gilbert Damping. *Europhys Lett.* 2003;61(3):354-360. Available from: <https://doi.org/10.1209/epl/i2003-00181-4>.
- [54] Sharma S, Dewhurst JK, Ambrosch-Draxl C, Kurth S, Helbig N, Pittalis S, et al. First-Principles Approach to Noncollinear Magnetism: Towards Spin Dynamics. *Phys Rev Lett.* 2007 May;98:196405. Available from: <https://doi.org/10.1103/PhysRevLett.98.196405>.
- [55] Peralta JE, Scuseria GE, Frisch MJ. Noncollinear Magnetism in Density Functional Calculations. *Phys Rev B.* 2007 Mar;75:125119. Available from: <https://doi.org/10.1103/PhysRevB.75.125119>.
- [56] Scalmani G, Frisch MJ. A New Approach to Noncollinear Spin Density Functional Theory beyond the Local Density Approximation. *J Chem Theory Comput.* 2012;8(7):2193-2196. Available from: <https://doi.org/10.1021/ct300441z>.
- [57] Bulik IW, Scalmani G, Frisch MJ, Scuseria GE. Noncollinear Density Functional Theory Having Proper Invariance and Local Torque Properties. *Phys Rev B.* 2013 Jan;87:035117. Available from: <https://doi.org/10.1103/PhysRevB.87.035117>.
- [58] Stratmann RE, Scuseria GE, Frisch MJ. Achieving linear scaling in exchange-correlation density functional quadratures. *Chem Phys Lett.* 1996;257(3):213 - 223. Available from: <http://www.sciencedirect.com/science/article/pii/0009261496006008>.
- [59] Burow AM, Sierka M. Linear Scaling Hierarchical Integration Scheme for the Exchange-Correlation Term in Molecular and Periodic Systems. *J Chem Theory Comput.* 2011;7(10):3097-3104. PMID: 26598153. Available from: <https://doi.org/10.1021/ct200412r>.

- [60] Visscher L, Dyall KG. Dirac-Fock Atomic Electronic Structure Calculations Using Different Nuclear Charge Distributions. *At Data Nucl Data Tables*. 1997;67:207–224. Available from: <https://doi.org/10.1006/adnd.1997.0751>.
- [61] Boettger JC. Approximate Two-Electron Spin-Orbit Coupling Term For Density-Functional-Theory DFT Calculations Using The Douglas-Kroll-Hess Transformation. *Phys Rev B*. 2000;62:7809–7815. Available from: <https://doi.org/10.1103/PhysRevB.62.7809>.
- [62] Schlegel HB, McDouall J. Do you have SCF stability and convergence problems? In: *Computational Advances in Organic Chemistry: Molecular Structure and Reactivity*. Springer; 1991. p. 167–185. Available from: https://link.springer.com/chapter/10.1007/978-94-011-3262-6_2.
- [63] Neese F. The ORCA program system. *Wiley Interdisciplinary Reviews: Computational Molecular Science*. 2012;2(1):73–78. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wcms.81>.
- [64] Neese F. Software update: the ORCA program system, version 4.0. *Wiley Interdisciplinary Reviews: Computational Molecular Science*. 2018;8(1):e1327. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wcms.1327>.
- [65] Parrish RM, Burns LA, Smith DGA, Simmonett AC, DePrince AE, Hohenstein EG, et al. Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. *Journal of Chemical Theory and Computation*. 2017;13(7):3185–3197. PMID: 28489372. Available from: <https://doi.org/10.1021/acs.jctc.7b00174>.
- [66] Bacskay GB. A quadratically convergent HartreeFock (QC-SCF) method. Application to closed shell systems. *Chem Phys*. 1981;61(3):385 – 404. Available from: <http://www.sciencedirect.com/science/article/pii/0301010481851567>.

- [67] Seeger R, Pople JA. Selfconsistent molecular orbital methods. XVIII. Constraints and stability in HartreeFock theory. *J Chem Phys.* 1977;66(7):3045–3050. Available from: <https://doi.org/10.1063/1.434318>.
- [68] Goings JJ, Ding F, Frisch MJ, Li X. Stability of the Complex Generalized Hartree-Fock Equations. *J Chem Phys.* 2015;142(15):154109. Available from: <http://dx.doi.org/10.1063/1.4918561>.
- [69] Takimoto Y, Vila FD, Rehr JJ. Real-Time Time-Dependent Density Functional Theory Approach for Frequency-Dependent Nonlinear Optical Response in Photonic Molecules. *J Chem Phys.* 2007;127(15):154114. Available from: <https://doi.org/10.1063/1.2790014>.
- [70] Krause P, Klamroth T, Saalfrank P. Molecular Response Properties from Explicitly Time-Dependent Configuration Interaction Methods. *J Chem Phys.* 2007;127(3):034107. Available from: <https://doi.org/10.1063/1.2749503>.
- [71] Ding F, Van Kuiken BE, Eichinger BE, Li X. An Efficient Method for Calculating Dynamical Hyperpolarizabilities Using Real-Time Time-Dependent Density Functional Theory. *J Chem Phys.* 2013;138:064104. Available from: <https://doi.org/10.1063/1.4790583>.
- [72] Goings JJ, Lestrange PJ, Li X. Real-Time Time-Dependent Electronic Structure Theory. *WIREs Computational Molecular Science.* 2018;8(1):e1341. Available from: <http://dx.doi.org/10.1002/wcms.1341>.
- [73] Uemoto M, Kuwabara Y, Sato SA, Yabana K. Nonlinear Polarization Evolution Using Time-Dependent Density Functional Theory. *J Chem Phys.* 2019;150(9):094101. Available from: <https://doi.org/10.1063/1.5068711>.
- [74] Frensley WR. Boundary Conditions for Open Quantum Systems Driven Far from Equilibrium. *Rev Mod Phys.* 1990 Jul;62:745–791. Available from: <https://doi.org/10.1103/RevModPhys.62.745>.

- [75] Chen G, Mukamel S. Reduced Electronic Density Matrices, Effective Hamiltonians, and Nonlinear Susceptibilities of Conjugated Polyenes. *J Chem Phys.* 1995;103(21):9355–9362. Available from: <https://doi.org/10.1063/1.469995>.
- [76] Magnus W. On the Exponential Solution of Differential Equations for a Linear Operator. *Commun Pur Appl Math.* 1954;7(4):649–673. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/cpa.3160070404>.
- [77] Castro A, Marques MAL, Rubio A. Propagators for the Time-Dependent KohnSham Equations. *J Chem Phys.* 2004;121(8):3425–3433. Available from: <https://doi.org/10.1063/1.1774980>.
- [78] Blanes S, Casas F. *A Concise Introduction to Geometric Numerical Integration*. New York, NY: Chapman and Hall/CRC; 2016.
- [79] Li X, Smith SM, Markevitch AN, Romanov DA, Levis RJ, Schlegel HB. A Time-Dependent Hartree-Fock Approach for Studying the Electronic Optical Response of Molecules in Intense Fields. *Phys Chem Chem Phys.* 2005;7:233–239. Available from: <http://doi.org/10.1039/B415849K>.
- [80] Williams-Young D, Goings JJ, Li X. Accelerating Real-Time Time-Dependent Density Functional Theory with a Non-Recursive Chebyshev Expansion of the Quantum Propagator. *J Chem Theory Comput.* 2016;12(11):5333–5338. Available from: <http://dx.doi.org/10.1021/acs.jctc.6b00693>.
- [81] Leforestier C, Bisseling RH, Cerjan C, Feit MD, Friesner R, Guldberg A, et al. A Comparison of Different Propagation Schemes for the Time Dependent Schrödinger Equation. *J Comput Phys.* 1991;94(1):59–80. Available from: [https://doi.org/10.1016/0021-9991\(91\)90137-A](https://doi.org/10.1016/0021-9991(91)90137-A).
- [82] Donati G, Wildman A, Caprasecca S, Lingerfelt DB, Lipparini F, Mennucci B, et al. Coupling Real-Time Time-Dependent Density Functional Theory with Polarizable Force Field. *J Phys Chem Lett.* 2017;8(21):5283–5289. Available from: <http://dx.doi.org/10.1021/acs.jpcllett.7b02320>.

- [83] Goings JJ, Li X. An Atomic Orbital Based Real-Time Time-Dependent Density Functional Theory for Computing Electronic Circular Dichroism Band Spectra. *J Chem Phys.* 2016;144(23):234102. Available from: <http://dx.doi.org/10.1063/1.4953668>.
- [84] Petrone A, Lingerfelt DB, Rega N, Li X. From Charge-Transfer to a Charge-Separated State: A Perspective from the Real-Time TDDFT Excitonic Dynamics. *Phys Chem Chem Phys.* 2014;16(44):24457–24465. Available from: <http://dx.doi.org/10.1039/C4CP04000G>.
- [85] Ding F, Guidez EB, Aikens CM, Li X. Quantum Coherent Plasmon in Silver Nanowires: A Real-Time TDDFT Study. *J Chem Phys.* 2014;140(24):244705. Available from: <http://dx.doi.org/10.1063/1.4884388>.
- [86] Donati G, Lingerfelt DB, Petrone A, Rega N, Li X. “Watching” Polaron Pair Formation from First-Principles Electron-Nuclear Dynamics. *J Phys Chem A.* 2016;120(37):7255–7261. Available from: <http://dx.doi.org/10.1021/acs.jpca.6b06419>.
- [87] Barron LD. *Molecular Light Scattering and Optical Activity.* 2nd ed. Cambridge, United Kingdom: Cambridge University Press; 2004.
- [88] Egidi F, Goings JJ, Frisch MJ, Li X. Direct Atomic-Orbital-Based Relativistic Two-Component Linear Response Method for Calculating Excited-State Fine Structures. *J Chem Theory Comput.* 2016;12(8):3711–3718. Available from: <http://dx.doi.org/10.1021/acs.jctc.6b00474>.
- [89] Williams-Young D, Egidi F, Li X. Relativistic Two-Component Particle-Particle Tamm-Dancoff Approximation. *J Chem Theory Comput.* 2016;12(11):5379–5384. Available from: <http://dx.doi.org/10.1021/acs.jctc.6b00833>.
- [90] Sen S, Lange KK, Tellgren EI. Excited States of Molecules in Strong Uniform and Nonuniform Magnetic Fields. *J Chem Theory Comput.* 0;0(0):Accepted. PMID: 31117478. Available from: <https://doi.org/10.1021/acs.jctc.9b00103>.

- [91] Kjærgaard T, Jansík B, Jørgensen P, Coriani S, Michl J. Gauge-Origin-Independent Coupled Cluster Singles and Doubles Calculation of Magnetic Circular Dichroism of Azabenzenes and Phosphabenzene Using London Orbitals. *J Phys Chem A*. 2007;111(44):11278–11286. PMID: 17518457. Available from: <https://doi.org/10.1021/jp0717261>.
- [92] Kjærgaard T, Jørgensen P, Thorvaldsen AJ, Salek P, Coriani S. Gauge-Origin Independent Formulation and Implementation of Magneto-Optical Activity within Atomic-Orbital-Density Based Hartree-Fock and Kohn-Sham Response Theories. *J Chem Theory Comput*. 2009;5(8):1997–2020. PMID: 26613143. Available from: <https://doi.org/10.1021/ct9001625>.
- [93] Zuev D, Vecharynski E, Yang C, Orms N, Krylov AI. New Algorithms for Iterative Matrix-Free Eigensolvers in Quantum Chemistry. *J Comput Chem*. 2015;36(5):273–284. Available from: <https://doi.org/10.1002/jcc.23800>.
- [94] Vecharynski E, Yang C, Xue F. Generalized Preconditioned Locally Harmonic Residual Method for Non-Hermitian Eigenproblems. *SIAM Journal on Scientific Computing*. 2016;38(1):A500–A527. Available from: <https://doi.org/10.1137/15M1027413>.
- [95] Davidson ER. The Iterative Calculation of a Few of the Lowest Eigenvalues and Corresponding Eigenvectors of Large Real-Symmetric Matrices. *J Comput Phys*. 1975;17:87. Available from: [https://doi.org/10.1016/0021-9991\(75\)90065-0](https://doi.org/10.1016/0021-9991(75)90065-0).
- [96] Morgan RB, Scott DS. Generalizations of Davidson’s Method for Computing Eigenvalues of Sparse Symmetric Matrices. *SIAM J Sci Statist Comput*. 1986;7:817–825. Available from: <https://doi.org/10.1137/0907054>.
- [97] Morgan RB. Generalizations of Davidson’s Method for Computing Eigenvalues of Large Non-Symmetric Matrices. *J Comput Phys*. 1992;101:287–291. Available from: <https://doi.org/10.1137/0907054>.
- [98] Kasper JM, Williams-Young DB, Vecharynski E, Yang C, Li X. A Well-Tempered Hybrid Method for Solving Challenging Time-Dependent Density Functional Theory

- (TDDFT) Systems. *J Chem Theory Comput.* 2018;14(4):2034–2041. Available from: <https://doi.org/10.1021/acs.jctc.8b00141>.
- [99] Larsen H, Jørgensen P, Olsen J, Helgaker T. HartreeFock and KohnSham atomic-orbital based time-dependent response theory. *J Chem Phys.* 2000;113(20):8908–8917. Available from: <https://doi.org/10.1063/1.1318745>.
- [100] Ekström U, Norman P, Carravetta V, Ågren H. Polarization Propagator for X-ray Spectra. *Phys Rev Lett.* 2006;97(14):143001. Available from: <https://doi.org/10.1103/PhysRevLett.97.143001>.
- [101] Linares M, Stafström S, Rinkevicius Z, Ågren H, Norman P. Complex Polarization Propagator Approach in the Restricted Open-Shell, Self-Consistent Field Approximation: The Near K-Edge X-ray Absorption Fine Structure Spectra of Allyl and Copper Phthalocyanine. *J Phys Chem B.* 2010;115(18):5096–5102. Available from: <https://doi.org/10.1021/jp103506g>.
- [102] Norman P, Bishop DM, Jørgen Aa Jensen H, Oddershede J. Near-Resonant Absorption in the Time-Dependent Self-Consistent Field and Multiconfigurational Self-Consistent Field Approximations. *J Chem Phys.* 2001;115(22):10323–10334. Available from: <https://doi.org/10.1063/1.1415081>.
- [103] Walker HF. Implementation of the GMRES Method using Householder Transformations. *SIAM J Sci Stat Comp.* 1988;9(1):152–163. Available from: <https://doi.org/10.1137/0909010>.
- [104] Peng B, Van Beeumen R, Williams-Young DB, Kowalski K, Yang C. Approximate Greens Function Coupled Cluster Method Employing Effective Dimension Reduction. *J Chem Theory Comput.* 2019;15(5):31853196. PMID: 30951302. Available from: <https://doi.org/10.1021/acs.jctc.9b00172>.
- [105] Grayce CJ, Harris RA. Magnetic-Field Density-Functional Theory. *Phys Rev A.* 1994 Oct;50:3089–3095. Available from: <https://link.aps.org/doi/10.1103/PhysRevA.50.3089>.

- [106] Tellgren EI, Teale AM, Furness JW, Lange KK, Ekström U, Helgaker T. Non-Perturbative Calculation of Molecular Magnetic Properties within Current-Density Functional Theory. *J Chem Phys.* 2014;140(3):034101. Available from: <https://doi.org/10.1063/1.4861427>.
- [107] Reimann S, Borgoo A, Tellgren EI, Teale AM, Helgaker T. Magnetic-Field Density-Functional Theory (BDFT): Lessons from the Adiabatic Connection. *J Chem Theory Comput.* 2017;13(9):4089–4100. PMID: 28768100. Available from: <https://doi.org/10.1021/acs.jctc.7b00295>.
- [108] Reimann S, Borgoo A, Austad J, Tellgren EI, Teale AM, Helgaker T, et al. Kohn-Sham Energy Decomposition for Molecules in a Magnetic Field. *Mol Phys.* 2019;117(1):97–109. Available from: <https://doi.org/10.1080/00268976.2018.1495849>.
- [109] Kokalj A. Computer Graphics and Graphical User Interfaces as Tools in Simulations of Matter at the Atomic Scale. *Comp Mater Sci.* 2003;28(2):155–168. Available from: [https://doi.org/10.1016/S0927-0256\(03\)00104-6](https://doi.org/10.1016/S0927-0256(03)00104-6).
- [110] Gonze X, Amadon B, Anglade PM, Beuken JM, Bottin F, Boulanger P, et al. ABINIT: First-Principles Approach to Material and Nanosystem Properties. *Comp Phys Comm.* 2009;180(12):2582–2615. Available from: <https://doi.org/10.1016/j.cpc.2009.07.007>.
- [111] Huang C, Pavone M, Carter EA. Quantum Mechanical Embedding Theory Based on a Unique Embedding Potential. *J Chem Phys.* 2011;134(15):154110. Available from: <https://doi.org/10.1063/1.3577516>.
- [112] Head-Gordon M, Pople JA, Frisch MJ. MP2 Energy Evaluation by Direct Methods. *Chem Phys Lett.* 1988;153(6):503 – 506. Available from: <http://www.sciencedirect.com/science/article/pii/0009261488852503>.
- [113] Christiansen O, Koch H, Jørgensen P. The Second-Order Approximate Coupled Cluster Singles and Doubles Model CC2. *Chem Phys Lett.* 1995;243(5):409 – 418. Available from: <http://www.sciencedirect.com/science/article/pii/000926149500841Q>.

- [114] Mukherjee D, Mukherjee PK. A response-function approach to the direct calculation of the transition-energy in a multiple-cluster expansion formalism. *Chem Phys.* 1979;39(3):325 – 335. Available from: <http://www.sciencedirect.com/science/article/pii/0301010479801536>.
- [115] Emrich K. An extension of the coupled cluster formalism to excited states (I). *Nuc Phys A.* 1981;351(3):379 – 396. Available from: <http://www.sciencedirect.com/science/article/pii/0375947481901792>.
- [116] Stanton JF, Bartlett RJ. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. *J Chem Phys.* 1993;98(9):7029–7039. Available from: <http://scitation.aip.org/content/aip/journal/jcp/98/9/10.1063/1.464746>.
- [117] Nascimento DR, DePrince III AE. Linear Absorption Spectra from Explicitly Time-Dependent Equation-of-Motion Coupled-Cluster Theory. *J Chem Theory Comput.* 2016;12(12):5834–5840. Available from: <http://doi.org/10.1021/acs.jctc.6b00796>.
- [118] Nascimento DR, DePrince III AE. Simulation of Near-Edge X-ray Absorption Fine Structure with Time-Dependent Equation-of-Motion Coupled-Cluster Theory. *J Phys Chem Lett.* 2017;8(13):2951–2957. Available from: <http://doi.org/10.1021/acs.jpcllett.7b01206>.
- [119] Schönhammer K, Gunnarsson O. Time-dependent approach to the calculation of spectral functions. *Phys Rev B.* 1978 Dec;18:6606–6614. Available from: <http://link.aps.org/doi/10.1103/PhysRevB.18.6606>.
- [120] Kvaal S. Ab initio quantum dynamics using coupled-cluster. *J Chem Phys.* 2012;136(19):194109. Available from: <http://scitation.aip.org/content/aip/journal/jcp/136/19/10.1063/1.4718427>.
- [121] Huber C, Klamroth T. Explicitly time-dependent coupled cluster singles doubles calculations of laser-driven many-electron dy-

- namics. J Chem Phys. 2011;134(5):054113. Available from: <http://scitation.aip.org/content/aip/journal/jcp/134/5/10.1063/1.3530807>.
- [122] Sato T, Pathak H, Orimo Y, Ishikawa KL. Communication: Time-dependent optimized coupled-cluster method for multielectron dynamics. J Chem Phys. 2018;148(5):051101. Available from: <https://doi.org/10.1063/1.5020633>.
- [123] Pedersen TB, Kvaal S. Symplectic integration and physical interpretation of time-dependent coupled-cluster theory. J Chem Phys. 2019;150(14):144106. Available from: <https://doi.org/10.1063/1.5085390>.
- [124] Klein K, Gauss J. Perturbative calculation of spin-orbit splittings using the equation-of-motion ionization-potential coupled-cluster ansatz. J Chem Phys. 2008;129(19):194106. Available from: <https://doi.org/10.1063/1.3013199>.
- [125] Epifanovsky E, Klein K, Stopkowicz S, Gauss J, Krylov AI. Spin-orbit couplings within the equation-of-motion coupled-cluster framework: Theory, implementation, and benchmark calculations. J Chem Phys. 2015;143(6):064102. Available from: <https://doi.org/10.1063/1.4927785>.
- [126] Cheng L, Wang F, Stanton JF, Gauss J. Perturbative treatment of spin-orbit-coupling within spin-free exact two-component theory using equation-of-motion coupled-cluster methods. J Chem Phys. 2018;148(4):044108. Available from: <https://doi.org/10.1063/1.5012041>.
- [127] Badala Viswanatha C, Helmich-Paris B, Httig C. Circularly polarised fluorescence and phosphorescence calculations on organic molecules using the approximate coupled-cluster model CC2. Phys Chem Chem Phys. 2018;20:21051–21061. Available from: <http://dx.doi.org/10.1039/C8CP03385D>.
- [128] Pathak H, Sahoo BK, Das BP, Vaval N, Pal S. Relativistic equation-of-motion coupled-cluster method: Application to closed-shell atomic systems. Phys Rev A. 2014 Apr;89:042510. Available from: <https://link.aps.org/doi/10.1103/PhysRevA.89.042510>.

- [129] Pathak H, Sasmal S, Nayak MK, Vaval N, Pal S. Relativistic equation-of-motion coupled-cluster method for the electron attachment problem. *Computational and Theoretical Chemistry*. 2016;1076:94 – 100. Available from: <http://www.sciencedirect.com/science/article/pii/S2210271X1500496X>.
- [130] Pathak H, Sasmal S, Nayak MK, Vaval N, Pal S. Relativistic equation-of-motion coupled-cluster method using open-shell reference wavefunction: Application to ionization potential. *J Chem Phys*. 2016;145(7):074110. Available from: <https://doi.org/10.1063/1.4960954>.
- [131] Akinaga Y, Nakajima T. Two-Component Relativistic Equation-of-Motion Coupled-Cluster Methods for Excitation Energies and Ionization Potentials of Atoms and Molecules. *J Phys Chem A*. 2017;121(4):827–835. PMID: 28118002. Available from: <https://doi.org/10.1021/acs.jpca.6b10921>.
- [132] Shee A, Saue T, Visscher L, Severo Pereira Gomes A. Equation-of-motion coupled-cluster theory based on the 4-component DiracCoulomb(Gaunt) Hamiltonian. Energies for single electron detachment, attachment, and electronically excited states. *J Chem Phys*. 2018;149(17):174113. Available from: <https://doi.org/10.1063/1.5053846>.
- [133] Wang Z, Tu Z, Wang F. Equation-of-Motion Coupled-Cluster Theory for Excitation Energies of Closed-Shell Systems with SpinOrbit Coupling. *J Chem Theory Comput*. 2014;10(12):5567–5576. PMID: 26583239. Available from: <https://doi.org/10.1021/ct500854m>.
- [134] Tu Z, Wang F, Li X. Equation-of-motion coupled-cluster method for ionized states with spin-orbit coupling. *J Chem Phys*. 2012;136(17):174102. Available from: <https://doi.org/10.1063/1.4704894>.
- [135] Yang DD, Wang F, Guo J. Equation of motion coupled cluster method for electron attached states with spinorbit coupling. *Chem Phys Lett*. 2012;531:236 – 241. Available from: <http://www.sciencedirect.com/science/article/pii/S0009261412002011>.

- [136] Asthana A, Liu J, Cheng L. Exact two-component equation-of-motion coupled-cluster singles and doubles method using atomic mean-field spin-orbit integrals. *J Chem Phys.* 2019;150(7):074102. Available from: <https://doi.org/10.1063/1.5081715>.
- [137] Nguyen DT, Steimle T, Linton C, Cheng L. Optical Stark and Zeeman Spectroscopy of Thorium Fluoride (ThF) and Thorium Chloride (ThCl). *J Phys Chem A.* 2019;123(7):1423–1433. PMID: 30668099. Available from: <https://doi.org/10.1021/acs.jpca.8b11853>.
- [138] Liu J, Cheng L. An atomic mean-field spin-orbit approach within exact two-component theory for a non-perturbative treatment of spin-orbit coupling. *J Chem Phys.* 2018;148(14):144108. Available from: <https://doi.org/10.1063/1.5023750>.
- [139] Gates M, Luszczek P, Abdelfattah A, Kurzak J, Dongarra J, Arturov K, et al. SLATE working note 2: C++ API for BLAS and LAPACK. Technical Report ICL-UT-17-03, Innovative Computing Laboratory, University of Tennessee; 2017.