Software Focus



The Dalton quantum chemistry program system

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Dalton is a powerful general-purpose program system for the study of molecular electronic structure at the Hartree–Fock, Kohn–Sham, multiconfigurational self-consistent-field, Møller–Plesset, configuration-interaction, and coupled-cluster levels of theory. Apart from the total energy, a wide variety of molecular properties may be calculated using these electronic-structure models. Molecular gradients and Hessians are available for geometry optimizations, molecular dynamics, and vibrational studies, whereas magnetic resonance and optical activity can be studied in a gauge-origin-invariant manner. Frequency-dependent molecular properties can be calculated using linear, quadratic, and cubic response theory. A large number of singlet and triplet perturbation operators are available for the study of one-, two-, and three-photon processes. Environmental effects may be included using various dielectric-medium and quantum-mechanics/molecular-mechanics models. Large molecules may be studied using linear-scaling and massively parallel algorithms. Dalton is distributed at no cost from http://www.daltonprogram.org for a number of UNIX platforms. © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

Dalton is a general-purpose program system for advanced quantum-chemical molecular electronic-structure calculations, distributed under a license agreement at no cost to the user. With Dalton, molecular systems may be studied using a variety of electronic-structure methods, including the Hartree–Fock (HF) and Kohn–Sham (KS) self-consistent-field (SCF) methods for wide applicability, the multiconfigurational SCF (MCSCF) method for high flexibility, and various coupled-cluster (CC) methods for high accuracy. At all these levels of theory, a wealth of molecular properties may be calculated, enabling the

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user of the program to study, for example, molecular structure, energetics, reactivity, spectroscopic parameters, linear, and nonlinear optical processes. Small systems may be accurately benchmarked using full configuration-interaction (FCI) techniques. Environmental effects may be incorporated at different levels of theory. For some electronic-structure models, large molecules can be studied using linear-scaling and massively parallel algorithms. In the present paper, we give an overview of the Dalton program system, with illustrations and emphasis on the Dalton2013 release.

ELECTRONIC-STRUCTURE MODELS

With the Dalton program, the electronic structure of a molecule can be described using all standard nonrelativistic wave-function and density-functional models of modern quantum chemistry. In particular, the wave function may be calculated using HF, MCSCF, configuration-interaction (CI), and CC theories. Using density-functional theory (DFT), calculations may be carried out with a range of KS exchange–correlation functionals. Dalton calculations are performed with generally contracted Gaussian-type orbitals (GTOs) with solid-harmonic or Cartesian angular factors as one-electron basis functions; some models also use two-electron functions for explicit correlation.

HF and KS SCF Theories

In Dalton, SCF calculations may be performed using a variety of optimization techniques. Apart from the traditional iterative Roothaan–Hall diagonalization method with direct-inversion-in-the-iterative-subspace (DIIS) convergence acceleration, the SCF energy may be optimized using a robust second-order trust-region method.[1] All calculations may be carried out in either serial or parallel manner. SCF calculations may also be carried out using the linear-scaling module discussed later.

With Dalton, KS studies may be performed with a variety of KS exchange–correlation functionals, including local-density-approximation (LDA) functionals, generalized-gradient-approximation (GGA) functionals such as BLYP and PBE, global hybrid functionals such as B3LYP and PBE0, and range-separated hybrid functionals such as CAM-B3LYP and r-CAM-B3LYP. Additional functionals may be obtained by combining the included functionals for exchange and correlation in new ways. Double-hybrid functionals such as B2PLYP and MPW2PLYP, with a second-order perturbation contribution, are available. For the GGA and hybrid functionals, the exchange–correlation potentials may be asymptotically corrected to ensure a proper long-range behavior, important for the study of Rydberg states using response theory.[2] Empirical DFT-D2 and DFT-D3 dispersion corrections may be applied. Dalton offers an implementation of spin-restricted and spin-unrestricted DFT for open-shell states.[3,4]

MCSCF Theory

For complicated electronic ground states characterized by static correlation and for valence-excited and core–hole states, MCSCF theory often provides the best solution. Dalton is characterized by an advanced MCSCF functionality with respect to both the construction of the MCSCF wave function and its optimization.[5–8] MCSCF ground- and excited-state wave functions can be constructed using the flexible concept of a generalized active space (GAS),[9] including the complete-active-space (CAS) and restricted-active-space (RAS)[10] models as special cases. Dalton uses robust and efficient second-order MCSCF optimization techniques, based on the concept of a trust region.

To recover dynamic as well as static correlation, MCSCF theory may be combined with *N*-electron valence state second-order perturbation theory (NEVPT2).[11] The NEVPT2 approach is similar to second-order CAS perturbation theory (CASPT2) but it is not affected by intruder-state problems.[12,13] All MCSCF and post-MCSCF multireference-CI calculations in Dalton are performed using the parallelized LUCITA module[14,15] with the wave function expanded either in configuration-state functions or in Slater determinants. As an important special case, FCI wave functions for benchmarking may be calculated using LUCITA.

CC Theory

For dynamical correlation, a variety of (spin-restricted) CC-based models have been implemented in Dalton: the coupled-cluster-singles (CCS) model, second-order-Møller–Plesset (MP2) theory, degeneracy-corrected second-order perturbation theory (DCPT2), the coupled-cluster-doubles (CCD) model, the coupled-cluster-singles-and-doubles (CCSD) model,[16,17] and the coupled-cluster-singles-doubles-perturbative-triples (CCSD(T)) models. Several ring-CCD and random-phase-approximation (RPA) models are also available,[18] including RPA with second-order screened exchange

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(RPA+SOSEX).[19] Frequency-dependent ground- and excited-state properties can be studied using several specially developed models.[20,21] In particular, Dalton contains the iterative CC2[22] and CC3[23] models for frequency-dependent properties and the noniterative CCSDR(3) triples-correction model[24] for excitation energies.

For faster basis-set convergence, the explicitly correlated MP2-R12/-F12, CCSD(T)(F12), and CC3(F12) models are available in Dalton.[25–27] For higher efficiency, Cholesky decomposition techniques have been implemented for the CCSD(T) energy[28] and for CC2 linear response properties.[29] Atomic subsystems can be defined by Cholesky decomposition to reduce the computational requirements of the CC models.[30]

Relativistic Corrections

Although Dalton is a nonrelativistic electronic-structure code based on the Schrödinger equation, it also has some functionality for incorporating the effects of relativity—in particular, effective core potentials may be used for energy and response functions.[31] Relativistic effects may also be included using Douglas–Kroll–Hess second-order one-electron scalar integrals.[31] When molecular response properties are calculated, the Breit–Pauli one- and two-electron spin–orbit operators may be included perturbatively.[32–34] Dalton offers scaled spin–orbit integrals and the atomic-mean-field approximation to the spin–orbit integrals[35] and parity-violation integrals.[36]

MOLECULAR PROPERTIES

Dalton is a versatile tool for studying molecular properties. By response theory, the linear, quadratic, and cubic response of a molecule to external perturbations, including geometrical distortions and electromagnetic fields, may be explored in detail and a wide variety of spectroscopic parameters can be calculated. In the following, the molecular properties implemented in Dalton are described.

Geometrical Properties

Molecular gradients (forces) and Hessians (force constants) may be calculated analytically at the HF, KS, and MCSCF[37,38] levels of theory, whereas analytical molecular gradients are available for the CCS, CC2, CCD, MP2, RPA, CCSD, and CCSD(T) models,[18,39] also in the frozen-core approximation. Numerical differentiation may be performed automatically for these quantities when an analytical implementation is not available.[40]

Dalton has an extensive functionality for exploring potential-energy surfaces by means of molecular gradients and Hessians. Minima can be determined using first-order (quasi-Newton) and second-order (Newton) methods.[41] Dalton also has several first- and second-order methods for determining saddle points (transition states), including mode following[42] and image minimization.[43] Geometry optimizations may be performed for excited states[44,45] and core-ionized states.[46] Potential-energy surfaces can be mapped by the calculation of intrinsic reaction coordinates. Born–Oppenheimer direct-dynamics studies can be performed by calculating classical molecular trajectories on the potential-energy surfaces, iteratively solving Newton's equation of motion for the atoms in the system, allowing dynamical studies of systems containing more than one hundred atoms.[47,48]

Dalton may be used to calculate molecular vibrational spectra. In addition to harmonic frequencies, infrared intensities are obtained in the double-harmonic approximation[49] and Raman intensities at a chosen frequency in the Placzek approximation. Dalton has an automated procedure for calculating rovibrationally averaged molecular geometries[50] and vibrational averages for molecular properties at the HF, KS, and MCSCF levels of theory.[40,51]

Magnetic Properties

Nuclear shielding and indirect nuclear spin–spin coupling constants of nuclear-magnetic-resonance (NMR) spectroscopy may be studied at many levels of theory, including DFT,[52–54] HF, and MCSCF theory,[55,56] the second-order polarization-propagator approximation (SOPPA),[57] and CC theory; for an illustration, see the KS calculation of spin–spin coupling constants in valinomycin in Figure 1. Likewise, the hyperfine coupling tensors,[58,59] electronic g tensors,[60] and zero-field splitting tensors[61] of electron-paramagnetic-resonance (EPR) spectroscopy may be calculated. A number of related properties such as spin–rotation tensors,[62] magnetizabilities,[63] rotational,[62] and vibrational[64] g tensors are available. In addition, several chiroptical properties may be studied: vibrational circular dichroism,[65] electronic circular dichroism,[66] optical rotation,[67] and vibrational Raman optical activity.[68]

In all calculations involving an external magnetic field, gauge-origin invariance is ensured by the use of London atomic orbitals, also known as gauge-including atomic orbitals. Alternatively, invariance may be ensured by the diamagnetic-zero version of the method of continuous transformation of the origin of the current density (CTOCD-DZ).[69]

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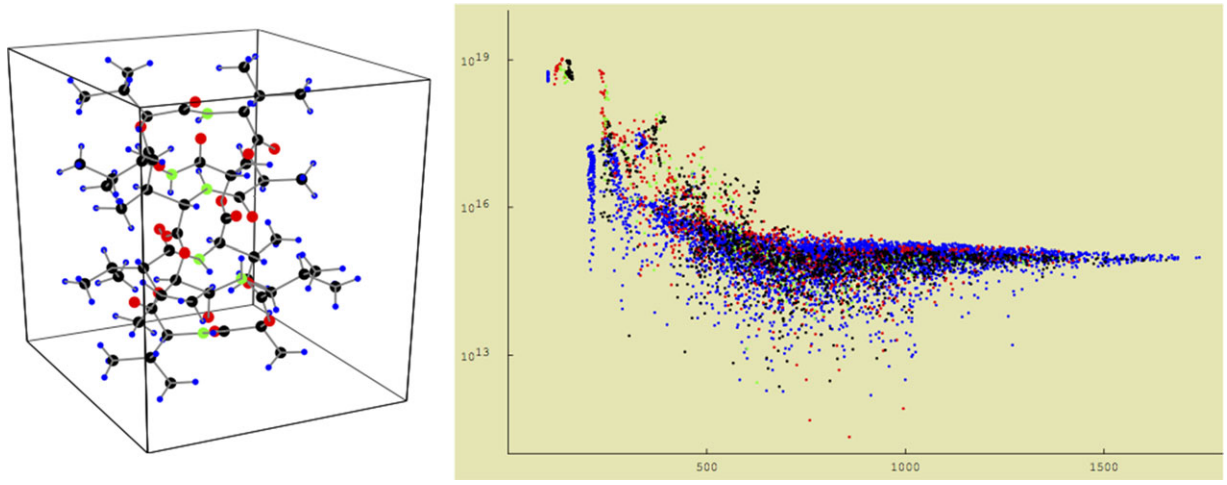


FIGURE 1 | The absolute value of the indirect spin–spin coupling constants (Hz, greater than 0.1 Hz) in valinomycin (left), on a logarithmic scale as a function of the internuclear distance (pm).[54] We have used blue, black, red, and green for the CH, CC, CO, and CN coupling constants, respectively. The spin–spin coupling constants have been calculated at the LDA/6-31G level of theory. (Reproduced with permission from Ref 54. Copyright 2004, John Wiley & Sons, Ltd.)

Frequency-Dependent Properties

Frequency-dependent linear response functions may be calculated at the HF, KS,[70] SOPPA,[71] and MCSCF levels of theory; at most of these levels of theory, quadratic and cubic response functions are also available. These functions contain a wealth of information not only about the reference state but also about other states of the molecular electronic system.[72] For example, the poles of a linear response function (such as the dipole–dipole polarizability tensor) correspond to excitation energies from the reference state (not necessarily the ground state), whereas the corresponding residues represent transition moments between the reference state and the excited states. Quadratic response functions[73] such as the first hyperpolarizability tensor provide information about nonlinear molecular response and two-photon processes—for example, coherent two-photon absorption[74,75] and two-photon absorption circular dichroism.[76] By means of quadratic response theory, phosphorescence phenomena such as spin-forbidden dipole transitions induced by spin–orbit coupling can be studied.[55,77] Cubic response functions[78–80] such as the second hyperpolarizability tensor give information about three-photon processes[81] and excited-state polarizabilities,[82] various higher-order spectroscopies such as second harmonic generation circular intensity difference,[83] as well as a wide range of birefringences. Many of these properties may be studied in the presence of an externally applied electric field.

Several response functions have been implemented for the CCS, CC2, and CCSD models, including ground-state expectation values,[84] excitation energies,[85] linear response functions,[86] quadratic response functions,[87] cubic response functions,[88] and their residues.[86,89] For the CC3 model, response properties including excitation energies have been implemented.[85,90] The double residues of the quadratic and cubic response functions allow first- and second-order properties of excited states—excited-state dipole moments and polarizabilities,[91] for example—to be obtained even for single-reference methods.

Dalton contains implementations of special methodologies for the calculation of a variety of X-ray spectroscopies, such as X-ray emission, absorption,[92] shake-up,[93] X-ray Raman,[94] and X-ray circular dichroism[95] spectroscopies. For HF and KS theories, this is accomplished with the 'static exchange' approximation[92] and the RPA-restricted channel technology, both of which are implemented with integral-direct methods, for applications to large systems such as polymers and surface adsorbates.

In standard response theory, the response functions become divergent under resonance conditions. Such divergences are unphysical, arising from the assumption of infinite lifetimes of excited states. In reality, relaxation mechanisms deplete the excited-state populations, making perturbation theory sound also under these conditions. Using the Ehrenfest theorem, an equation of motion for state vectors that mimics the inclusion of relaxation in density-matrix theory by the Liouville equation has been established.[96] The resulting complex-polarization-propagator (CPP) approach has been implemented at the HF, KS, MCSCF, and CC levels of theory.[96–100] The CPP

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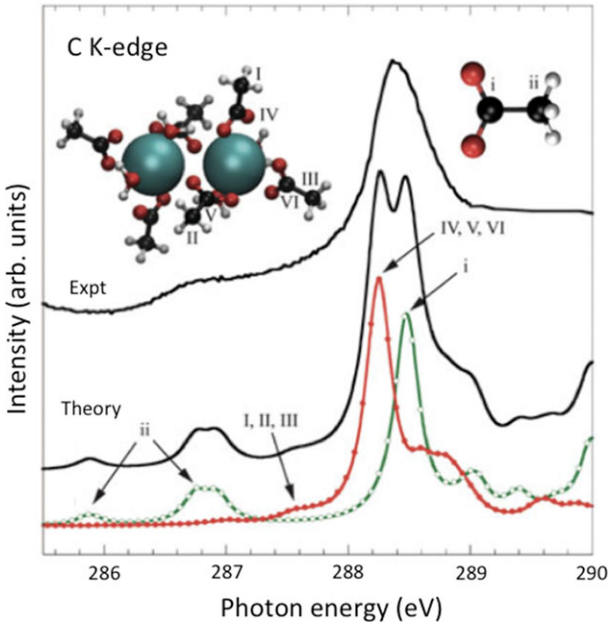


FIGURE 2 | Near-edge X-ray absorption fine structure (NEXAFS) study of Gd acetate nanoparticles. The experimental spectrum (top) is compared with the sum of the theoretical spectra (black) for isolated acetate (green) and a coordination complex (red). (Reproduced with permission from Ref 105. Copyright 2012, Springer.)

response functions are resonance convergent and complex valued, providing a direct means of addressing spectroscopies carried out in regions of electronic resonances such as electronic circular dichroism,[101] resonance Raman,[102] magnetic circular dichroism,[103] and vis/UV/X-ray absorption[98,104] spectroscopies. In Figure 2, we have plotted the NEXAFS linear absorption cross-section of Gd acetate nanoparticles, extracted from the imaginary part of the KS CPP electric-dipole polarizability.[105] This calculation addresses the spectral region of the carbon K-edge, demonstrating the universal treatment of the spectrum in CPP theory.

Environmental Effects

In Dalton, environmental effects may be included in quantum-chemical calculations either by treating the environment as a homogeneous dielectric continuum or by describing it at the level of polarizable molecular mechanics. In the simplest continuum approach, the self-consistent-reaction-field (SCRF) approach,[106–108] the solute is placed in a spherical cavity in the dielectric medium. The SCRF method has been implemented for the HF, KS, CC2, CCSD, MCSCF, and SOPPA models and may be applied to linear, quadratic, and cubic response functions (up to quadratic response functions for the CC models) as well as for geometrical properties (molecular gradients and Hessians) and spin-resonance properties.[109–114] In the more elaborate polarized-dielectric-continuum model (PCM),[115] the solute is placed in a molecule-shaped cavity, thereby improving the solute–solvent description. Solvent effects at the level of PCM may be evaluated using the HF, KS, or MCSCF models and are available for properties up to the level of cubic response theory[116–118] and for molecular gradients. The SCRF and PCM solvation models have both been implemented in a general nonequilibrium formalism.

Using the polarizable-embedding (PE) scheme,[119–125] the environment may be treated as a structured and polarizable medium—that is, the discrete nature of the environment is retained and is described by distributed multipoles and anisotropic dipole–dipole polarizabilities. The PE method may be applied at the HF, KS, MP2, SOPPA, CCSD, or CC2 levels of theory and properties up to linear response may be evaluated. In addition, quadratic-response properties are available at the HF and KS levels.

Figure 3 illustrates the calculation of biophotonics properties with Dalton. The left insert shows an X-ray structure of channelrhodopsin, highlighting the chromophore embedded in the binding pocket of the protein. Using the PE method, the effect of the protein on the chromophore is described by representing the protein by distributed multipoles and (anisotropic) polarizabilities, retaining a quantum-mechanical description of the chromophore itself. The calculated embedding potential is highly anisotropic, significantly affecting the optical properties of the chromophore as illustrated by the one- and two-photon absorption spectra calculated at different levels of theory: by neglecting the protein environment entirely ('vacuum'), by adjusting the chromophore geometry to that inside the protein ('geometry'), by including the electrostatics but neglecting protein relaxation ('electrostatics'), and by including both electrostatics and protein relaxation ('polarization').

LARGE MOLECULES

For large molecules, containing up to more than a thousand atoms, Dalton contains a massively parallel, linear-scaling module for the HF, KS, and MP2 electronic-structure models; CCSD energies are also available in a massively parallel but not linear-scaling manner. For large molecules, it is essential to employ stable energy-optimization schemes so as to avoid divergence or convergence to spurious solutions, which is achieved by combining the robust

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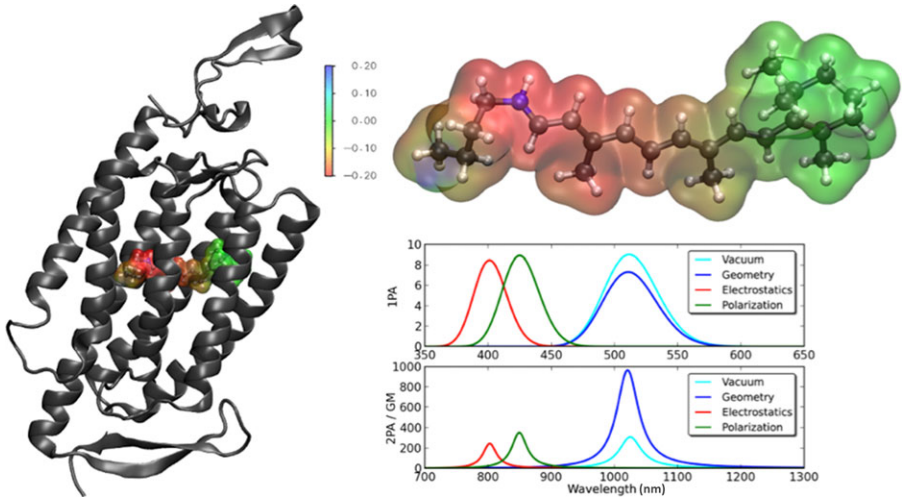


FIGURE 3 | One- and two-photon absorption spectra for channelrhodopsin calculated using the polarizable embedding method implemented in Dalton. The insert on the top of the right hand side shows the protein embedding potential projected onto the molecular surface.

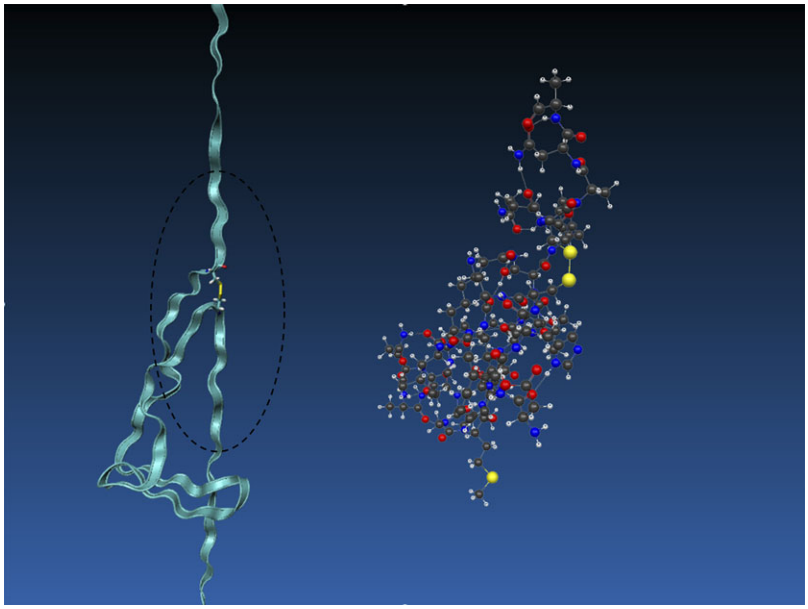


FIGURE 4 | Left: The titin-I27 domain highlighting the disulfide bridging bond and a schematic representation of the stretching of the polyprotein strain by the aid of the atomic force microscopy; right: the titin-I27SS model, designed to model the redox-active site in the titin-I27 domain.

three-level/augmented Roothaan–Hall method with a line-search trust-region technique.[126–128] Fock/KS matrices and integrals are calculated by combining *J*-engine and density-fitting techniques with linear-scaling techniques such as the continuous fast multipole method (CFMM)[129,130] and the linear-scaling exchange (LinK) method.[131,132] This new SCF module is efficient also for medium-sized molecules, often reducing CPU time by an order of magnitude or more relative to optimizations carried out with the standard module—enabling, for example, studies of dynamics for systems containing more than 100 atoms.[48]

To illustrate the capabilities of Dalton for large molecules, we consider two systems—namely, the 168-atom valinomycin molecule and the 392-atom titin-I27SS model,[38] see Figure 4. For valinomycin, geometry optimizations were conducted at the BP86/6-31G** and CAM-B3LYP/6-31G** levels of theory. Using 64 cores on eight 2.60 GHz Intel Xeon E5-2670 nodes, the geometry optimizations converged

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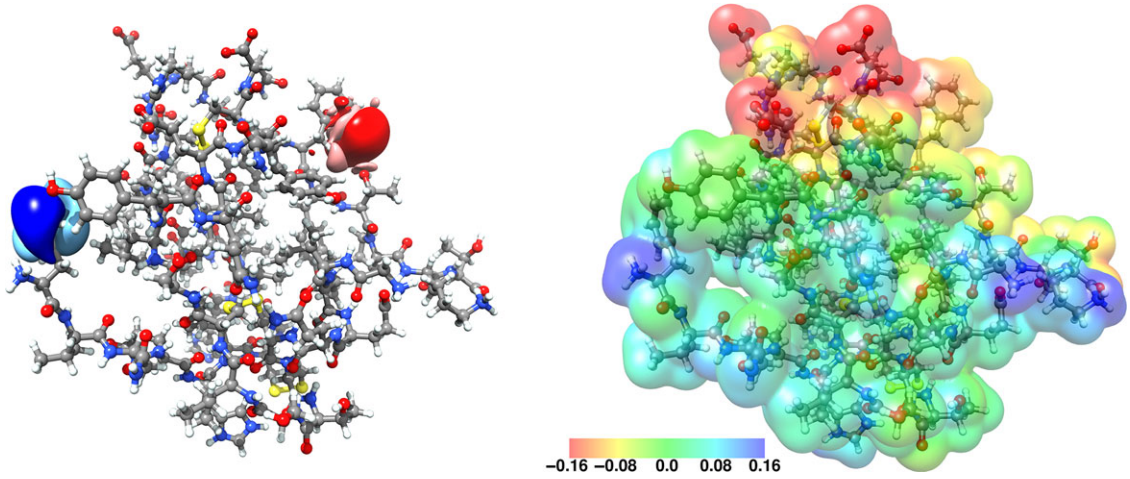


FIGURE 5 | MP2 study of insulin (787 atoms) in the cc-pVDZ basis (7,604 orbitals). Left: Localized orbitals obtained by minimizing the second power of the orbital variances. The least local occupied (blue) and least local virtual (red) orbitals are plotted using orbital contour values of 0.01 a.u. Right: MP2 electrostatic potential calculated using the DEC scheme plotted on an isodensity surface (0.001 a.u.). The values are indicated by the color box (a.u.).

in 33 and 30 geometry steps, respectively. These optimizations took a total of 67 and 219 min, with an average of 2.0 and 7.3 min per geometry step, respectively. For the titin model, a single geometry step takes 25 min at the CAM-B3LYP/6-31G** level of theory.

Dalton has linear-scaling HF and KS modules for a number of molecular properties,[133,134] including polarizabilities, excitation energies, one- and two-photon absorption spectra, magnetic-circular-dichroism parameters,[135,136] and NMR shielding constants. Excited-state geometry optimizations are available.[45] It is also possible to generate various absorption spectra using damped response theory.[100,137]

To recover dynamical correlation in large molecules, Dalton utilizes a novel algorithm for generating highly local HF orbitals.[138,139] Such orbitals constitute the basis for the linear-scaling, massively parallel MP2 implementation in Dalton, which exploits the inherent locality of dynamical correlation in the Divide–Expand–Consolidate (DEC) strategy.[140–142]

As an illustration, we consider the calculation of the MP2 electrostatic potential of insulin. The HF orbitals were localized by minimizing the sum of the second powers of the orbital variances, generating a set of local occupied orbitals and a set of local virtual orbitals.[138] Even the least local orbitals from this set, which are plotted in Figure 5 (left), are localized to small regions of the insulin molecule. The use of these local orbitals allows the inherently local electron correlation effects to be described efficiently using the DEC scheme. In Figure 5 (right), the DEC scheme was used to calculate the MP2 electrostatic potential for insulin, which may be used to identify areas of reactivity.

DALTON HISTORY

The development that led to Dalton began in the early 1980s, as a collaboration between Scandinavian research groups at the Universities of Aarhus (H. J. Aa. Jensen, P. Jørgensen, J. Olsen), Oslo (T. Helgaker), and Uppsala (H. Ågren). Up to the mid 1990s, several programs that later became the Dalton code were run separately from a simple Bourne shell script. Molecular integrals over GTOs were calculated using the HERMIT code,[143] HF and MCSCF wave functions were optimized using the SIRIUS code,[1] whereas frequency-independent and -dependent molecular properties were calculated using the ABACUS[144] and RESPONS[145] codes, respectively.

The separate HERMIT, SIRIUS, ABACUS, and RESPONS codes were merged in 1995 and released as **Dalton 1.0** in 1997. This first release was essentially an MCSCF code with emphasis on molecular properties, including molecular gradients, Hessians, NMR properties, and linear, quadratic, and cubic response theory. **Dalton 1.1** was released later in 1997, with bug fixes and performance improvements.

The next major release was **Dalton 1.2** in 2001, which included integral-direct CC functionality that had been developed since the early 1990s[16] and properties up to cubic response. Other important additions were SOPPA, nonequilibrium solvation, and vibrational averaging of molecular properties. The release

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included a new integral module ERI, developed for vector computers and integral-driven CC theory.[17]

In 2005, **Dalton 2.0** was released with a DFT module with functionality for molecular gradients and Hessians, NMR and EPR parameters, linear and quadratic response properties, based on an initial DFT implementation from 2000.[52] In addition, Dalton 2.0 included NEVTP2 and MP2–R12 modules and numerous other additions and improvements.

The **Dalton2011** release introduced a new module for linear-scaling HF and KS calculations of large systems, using density fitting and CFMM techniques. In addition, Dalton2011 introduced a variety of additions and improvements to existing modules (CC3 and CCSD-R12), Cholesky techniques in the CC module,[146] range-separated functionals,[147] an excitation-energy diagnostic for DFT,[148] and an atomic integral-direct implementation of the SOPPA[149] and RPA(D)[150] models. For the treatment of environmental effects, the PCM module was introduced.

In the **Dalton2013** release, the linear-scaling module has been extended significantly to incorporate local orbitals, the DEC-MP2 model, magnetic properties for HF and KS theories, and molecular dynamics. New massively parallel techniques have been introduced for SCF, DEC-MP2, and CCSD energies. Parallel MCSCF techniques have been introduced, extending the limit for MCSCF configuration-space sizes by at least an order of magnitude. Spin-multiplet[151] and spin-flip[152] density-functional response-theory methodologies, based on collinear and noncollinear exchange–correlation kernels, have been introduced, allowing computations of excited states with double-excitation character and various low-spin ground states.

PROGRAM STRUCTURE

Program Modules

Dalton consists of several modules, developed more or less independently. The HERMIT module calculates not only the integrals needed for energies but also for a large number of molecular properties, including all one- and two-electron integrals of the Breit–Pauli Hamiltonian. The ERI module is a vectorized and distribution-oriented integral generator that is invoked in certain calculations—in particular, in integral-direct CC calculations.

The SIRIUS module contains the (MC)SCF energy optimization code, whereas the CC module performs CC optimizations and property calculations. The LUCITA module performs large-scale CI calculations for general CI expansions and serves the MCSCF module with parallel evaluation of configuration vectors and density matrices. The DFT module performs the numerical exchange–correlation integration and serves the SIRIUS module with the required KS matrix elements.

The ABACUS module evaluates second-order properties for the (MC)SCF models—in particular, second-order static molecular properties in which the basis set depends on the applied perturbation. The RESPONS module is a general-purpose code for evaluating response functions, up to cubic response for (MC)SCF wave functions, quadratic, and cubic response for KS theory, and linear response for the SOPPA model. Linear-scaling calculations are performed with the LSDALTON module.

Programming Details and Language

The Dalton program is written in FORTRAN 77, FORTRAN 90, and C, with machine dependencies isolated using C preprocessor directives. All floating-point computations are performed in 64-bit precision but the code takes advantage of 32-bit precision to reduce integer storage requirements in some sections.

The parallelization of the regular Dalton SCF modules for small molecules has been done exclusively using MPI and scales (for sufficiently large systems) with up to 90% efficiency on 1000 processors,[153,154] even demonstrating superlinear scaling.[155] Also the CI routines have been parallelized using MPI.[15] The Dalton SCF modules for large molecules have been parallelized in a hybrid MPI/OpenMP scheme.

Hardware/Software Supported

Dalton runs on a variety of UNIX systems. The current release of the program has been tested on IBM-AIX, Linux, and OS X but is easily ported to other UNIX systems.

Program Distribution

The Dalton source code is distributed to users at no cost. Three types of licenses are available: personal, site, and benchmark. With all licenses, the copyright to the code remains with the authors and is not put in the public domain—in particular, the source and binary code may not be redistributed. Furthermore, no fee may be charged for the use of Dalton. For copies of Dalton distributed with a site license, users may not access the source and object files. Benchmark licenses differ from personal and site licenses in that access is given to Dalton only for a restricted period

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of time. One year after its release, more than 700 personal and 150 site licenses had been issued for Dalton 2011.

User Support

Dalton is distributed with limited user support. The code is installed using CMake with an automatic adaptation to supported platforms. Dalton is distributed with a cross-referenced manual and a test suite comprising more than 400 test jobs. Information about patches, releases, and other updates are provided on the Dalton forum (http://daltonprogram.org/forum), where users can also exchange experiences, view tutorials and seek help on installing and using the Dalton programs.

CONCLUSION

We have presented the Dalton quantum chemistry program system—a highly flexible general-purpose code for molecular electronic-structure calculations. As a result of 30 years of continuous and vigorous development by a large number of authors, Dalton offers today not only a large selection of molecular electronic-structure models (including all standard models) but also the ability to calculate an exceptionally broad range of molecular properties from these models. In this manner, Dalton constitutes a unique tool for quantum-mechanical calculations of molecular systems, ranging from linear-scaling studies of large systems to high-accuracy benchmark studies on small systems.

REFERENCES

1. Jensen HJAa, Ågren H. *Documentation of SIRIUS: A General Purpose Direct Second Order MCSCF Program*. Technical Notes TN783, TN784, TN785. Department of Quantum Chemistry, University of Uppsala, Uppsala, Sweden; 1986.
2. Teale AM, De Proft F, Tozer DJ. Orbital energies and negative electron affinities from density functional theory: insight from the integer discontinuity. *J Chem Phys* 2008, 129:044110.
3. Rinkevicius Z, Tunell I, Salek P, Vahtras O, Ågren H. Restricted density functional theory of linear time-dependent properties in open-shell molecules. *J Chem Phys* 2003, 119:34–46.
4. Oprea O, Telyatnyk L, Rinkevicius Z, Vahtras O, Ågren H. Time-dependent density functional theory with the generalized restricted-unrestricted approach. *J Chem Phys* 2006, 124:174103.
5. Jensen HJAa, Ågren H. MCSCF optimization using the direct, restricted step, second order norm-extended optimization method. *Chem Phys Lett* 1984, 110:140–144.
6. Jensen HJAa, Ågren H. A direct, restricted-step, 2nd-order MC SCF program for large-scale ab initio calculations. *Chem Phys* 1986, 104:229–250.
7. Jensen HJAa, Jørgensen P, Ågren H. Efficient optimization of large-scale MCSCF wave-functions with a restricted step algorithm. *J Chem Phys* 1987, 87:451–466.
8. Jensen HJAa, Jørgensen P, Ågren H, Olsen J. 2nd-order Møller–Plesset perturbation-theory as a configuration and orbital generator in multiconfiguration self-consistent-field calculations. *J Chem Phys* 1988, 88:3834–3839 and 89:5354–5354.
9. Olsen J. The initial implementation and applications of a general active space coupled cluster method. *J Chem Phys* 2000, 113:7140–7148.
10. Olsen J, Roos BO, Jørgensen P, Jensen HJAa. Determinant based algorithms for complete and restricted configuration interaction spaces. *J Chem Phys* 1988, 89:2185–2192.
11. Havenith RWA, Taylor PR, Angeli C, Cimiraglia R, Ruud K. Calibration of the n-electron valence state perturbation theory approach. *J Chem Phys* 2004, 120:4619–4625.
12. Dyall KG. The choice of a zeroth-order Hamiltonian for second-order perturbation theory with a complete active space self-consistent-field reference function. *J Chem Phys* 1995, 102:4909–4918.
13. Angeli C, Cimiraglia R, Evangelisti S, Leininger T, Malrieu JP, Introduction of n-electron valence states for multireference perturbation theory. *J Chem Phys* 2001, 114:10252–10264.
14. Olsen J, *LUCITA, A General Active Configuration Interaction Code*. Aarhus University, Aarhus, Denmark; 2000.
15. Knecht S, Jensen HJAa, Fleig T. Large-scale parallel configuration interaction. I. Nonrelativistic and scalar-relativistic general active space implementation with application to $(Rb\text{-}Ba)^+$. *J Chem Phys* 2008, 128:014108.
16. Koch H, Christiansen O, Kobayashi R, Jørgensen P, Helgaker T. A direct atomic orbital driven implementation of the coupled cluster singles and doubles (CCSD) model. *Chem Phys Lett* 1994, 228:233–238.
17. Koch H, Sánchez de Merás A, Helgaker T, Christiansen O. The integral-direct coupled cluster singles and doubles model. *J Chem Phys* 1996, 104:4157–4165.
18. Rekkedal J, Coriani S, Iozzi MF, Teale AM, Helgaker T, Pedersen TB. Communcation: analytic gradients in the random-phase approximation. *J Chem Phys* 2013, 139:081101.

 © 2013 John Wiley & Sons, Ltd.

19. Grüneis A, Marsman M, Harl J, Schimka L, Kresse G. Making the random phase approximation to electronic correlation accurate. *J Chem Phys* 2009, 131:154115.
20. Pedersen TB, Koch H. Coupled cluster response functions revisited. *J Chem Phys* 1997, 106:8059–8072.
21. Christiansen O, Hättig C, Jørgensen P. Response functions from Fourier component perturbation theory applied to a time-averaged quasienergy. *Int J Quantum Chem* 1998, 68:1–52.
22. Christiansen O, Koch H, Jørgensen P. The second order approximate coupled cluster singles and doubles model CC2. *Chem Phys Lett* 1995, 243:409–418.
23. Christiansen O, Koch H, Jørgensen P. Response functions in the CC3 iterative triple excitation model. *J Chem Phys* 1995, 103:7429–7441.
24. Christiansen O, Koch H, Jørgensen P. Perturbative triple excitation corrections to coupled cluster singles and doubles excitation energies. *J Chem Phys* 1996, 105:1451–1459.
25. Klopper W, Samson CCM. Explicitly correlated second-order Møller–Plesset methods with auxiliary basis sets. *J Chem Phys* 2002, 116:6397–6410.
26. Samson CCM, Klopper W, Helgaker, T. Computation of two-electron Gaussian integrals for wave functions including the correlation factor $r_{12}\exp(-\gamma r^2_{12})$. *Comp Phys Commun* 2002, 149:1–10.
27. Tew DP, Klopper W, Neiss C, Hättig C. Quintuple-zeta quality coupled-cluster correlation energies with triple-zeta basis sets. *Phys Chem Chem Phys* 2007, 9:1921–1930.
28. Cacheiro JL, Pedersen TB, Fernández B, Sánchez de Merás A, Koch H. The CCSD(T) model with Cholesky decomposition of orbital energy denominators. *Int J Quantum Chem* 2011, 111:349–355.
29. Pedersen TB, Sánchez de Merás AMJ, Koch H. Polarizability and optical rotation calculated from the approximate coupled cluster singles and doubles CC2 linear response theory using Cholesky decompositions. *J Chem Phys* 2004, 120:8887–8897.
30. Sánchez de Merás AMJ, Koch H, Cuesta IG, Boman L. Cholesky decomposition-based definition of atomic subsystems in electronic structure calculations. *J Chem Phys* 2010, 132:204105.
31. Norman P, Schimmelpfennig B, Ruud K, Jensen HJAa, Ågren H. Relativistic effects on linear and nonlinear polarizabilities studied by effective-core potential, Douglas–Kroll, and Dirac–Hartree–Fock response theory. *J Chem Phys* 2002, 116:6914–6923.
32. Coriani S, Helgaker T, Jørgensen P, Klopper W. A closed-shell coupled-cluster treatment of the Breit–Pauli first-order relativistic energy correction. *J Chem Phys* 2004, 121:6591–6598.
33. Vahtras O, Ågren H, Jørgensen P, Jensen HJAa, Helgaker T, Olsen J. Spin–orbit coupling constants in a multiconfiguration linear response approach. *J Chem Phys* 1992, 96:2118–2126.
34. Vahtras O, Ågren H, Jørgensen P, Jensen HJAa, Helgaker T, Olsen J. Multiconfigurational quadratic response functions for singlet and triplet perturbations: the phosphorescence lifetime of formaldehyde. *J Chem Phys* 1992, 97:9178–9187.
35. Ruud K, Schimmelpfennig B, Ågren H. Internal and external heavy-atom effects on phosphorescence radiative lifetimes calculated using a mean-field spin-orbit Hamiltonian. *Chem Phys Lett* 1999, 310:215–221.
36. Hennum AC, Helgaker T, Klopper W. Parity-violating interaction in H_2O_2 calculated from density-functional theory. *Chem Phys Lett* 2002, 354:274–282.
37. Helgaker TU, Almlöf J, Jensen HJAa, Jørgensen P. Molecular Hessians for large-scale MCSCF wave functions. *J Chem Phys* 1986, 84:6266–6279.
38. Reine S, Krapp A, Iozzi MF, Bakken V, Helgaker T, Pawłowski F, Sałek P. An efficient density-functional-theory force evaluation for large molecular systems. *J Chem Phys* 2010, 133:044102.
39. Hald, K, Halkier A, Jørgensen P, Coriani S, Hättig C, Helgaker T. A Lagrangian, integral-density direct formulation and implementation of the analytic CCSD and CCSD(T) gradients. *J Chem Phys* 2003, 118:2985–2998.
40. Ruden TA, Taylor PR, Helgaker T. Automated calculation of fundamental frequencies: application to AlH_3 using the coupled-cluster singles-and-doubles with perturbative triples method. *J Chem Phys* 2003, 119:1951–1960.
41. Bakken V, Helgaker T. The efficient optimization of molecular geometries using redundant internal coordinates. *J Chem Phys* 2002, 117:9160–9174.
42. Jensen HJAa, Jørgensen P, Helgaker T. Systematic determination of MCSCF equilibrium and transition structures and reaction paths. *J Chem Phys* 1986, 85:3917–3929.
43. Helgaker T. Transition-state optimizations by trust-region image minimization. *Chem Phys Lett* 1991, 182:503–510.
44. Cesar A, Ågren H, Helgaker T, Jørgensen P, Jensen HJAa. Excited state structures and vibronic spectra of H_2CO^+, $HDCO^+$ and D_2CO^+ using molecular gradient and Hessian techniques. *J Chem Phys* 1991, 95:5906–5917.
45. Coriani S, Kjærgaard T, Jørgensen P, Ruud K, Huh J, Berger R. An atomic-orbital-based Lagrangian approach for calculating geometric gradients of linear response properties. *J Chem Theory Comp* 2010, 6, 1020–1047.
46. Norman P, Ågren H. Geometry optimization of core electron excited molecules. *J Mol Struct: THEOCHEM* 1997, 401:107–115.

 © 2013 John Wiley & Sons, Ltd.

47. Helgaker T, Uggerud E, Jensen HJAa. Integration of the classical equations of motion on ab initio molecular potential energy surfaces using gradients and Hessians: application to translational energy release upon fragmentation. *Chem Phys Lett* 1990, 173:145–150.
48. Rybkin VV, Simakov AO, Bakken V, Reine SS, Kjærgaard T, Helgaker T, Uggerud E. Insights into the dynamics of evaporation and proton migration in protonated water clusters from large-scale Born–Oppenheimer direct dynamics. *J Comput Chem* 2013, 34:533–544.
49. Helgaker TU, Jensen HJAa, Jørgensen P. Analytical calculation of MCSCF dipole-moment derivatives. *J Chem Phys* 1986, 84:6280–6284.
50. Åstrand P-O, Ruud K, Taylor PR. Calculation of the vibrational wave function of polyatomic molecules. *J Chem Phys* 2000, 112:2655–2667.
51. Ruud K, Åstrand, P-O, Taylor PR. An efficient approach for calculating vibrational wave functions and zero-point vibrational corrections to molecular properties of polyatomic molecules. *J Chem Phys* 2000, 112:2668–2683.
52. Helgaker T, Wilson PJ, Amos RD, Handy NC. Nuclear shielding constants by density functional theory with gauge including atomic orbitals. *J Chem Phys* 2000, 113:2983–2989.
53. Helgaker T, Watson M, Handy NC. Analytical calculation of nuclear magnetic resonance indirect spin–spin coupling constants at the generalized gradient approximation and hybrid levels of density-functional theory. *J Chem Phys* 2000, 113:9402–9409.
54. Watson MA, Sałek P, Macak P, Jaszuński M, Helgaker T. The calculation of indirect nuclear spin-spin coupling constants in large molecules. *Chem Eur J* 2004, 10:4627–4639.
55. Vahtras O, Ågren H, Jørgensen P, Jensen HJAa, Padkjær SB, Helgaker T. Indirect nuclear spin–spin coupling constants from multiconfiguration linear response theory. *J Chem Phys* 1992, 96:6120–6125.
56. Ruud K, Helgaker T, Kobayashi R, Jørgensen P, Bak KL, Jensen HJAa. Multiconfigurational self-consistent field calculations of nuclear shieldings using London atomic orbitals. *J Chem Phys* 1994, 100:8178–8185.
57. Enevoldsen T, Oddershede J, Sauer SPA. Correlated calculations of indirect nuclear spin–spin coupling constants using second order polarization propagator approximations: SOPPA and SOPPA(CCSD). *Theor Chem Acc* 1998, 100:275–284.
58. Fernández B, Jørgensen P, Byberg J, Olsen J, Helgaker T, Jensen HJAa. Spin polarization in restricted electronic structure theory: multiconfiguration self-consistent-field calculations of hyperfine coupling constants. *J Chem Phys* 1992, 97:3412–3419.
59. Rinkevicius Z, Telyatnyk L, Vahtras O, Ågren H. Density functional theory for hyperfine coupling constants with the restricted-unrestricted approach. *J Chem Phys* 2004, 121:7614–7623.
60. Vahtras O, Minaev B, Ågren H. Ab initio calculations of electronic g-factors by means of multiconfiguration response theory. *Chem Phys Lett* 1998, 281:186–192.
61. Vahtras O, Loboda O, Minaev B, Ågren H, Ruud K. Ab initio calculations of zero-field splitting parameters. *Chem Phys* 2002, 279:133–142.
62. Gauss J, Ruud K, Helgaker T. Perturbation-dependent atomic orbitals for the calculation of spin-rotation constants and rotational *g* tensors. *J Chem Phys* 1996, 105:2804–2812.
63. Ruud K, Helgaker T, Bak KL, Jørgensen P, Jensen HJAa. Hartree–Fock limit magnetizabilities from London orbitals. *J Chem Phys* 1993, 99: 3847–3859.
64. Bak KL, Sauer SPA, Oddershede J, Ogilvie JF. The vibrational g factor of dihydrogen from theoretical calculation and analysis of vibration-rotational spectra. *Phys Chem Chem Phys* 2005, 7:1747–1758.
65. Bak KL, Jørgensen P, Helgaker T, Ruud K, Jensen HJAa. Gauge-origin independent multiconfigurational self-consistent-field theory for vibrational circular dichroism. *J Chem Phys* 1993, 98:8873–8887.
66. Bak KL, Hansen AaE, Ruud R, Helgaker T, Olsen J, Jørgensen P. Ab-initio calculation of electronic circular dichroism for trans-cyclooctene using London atomic orbitals. *Theor Chim Acta* 1995, 90: 441–458.
67. Ruud K, Helgaker T. Optical rotation studied by density-functional and coupled-cluster methods. *Chem Phys Lett* 2002, 352:533–539.
68. Helgaker T, Ruud K, Bak KL, Jørgensen P, Olsen J. Vibrational Raman optical activity calculations using London atomic orbitals. *Faraday Discuss* 1994, 99:165–180.
69. Ligabue A, Sauer SPA, Lazzeretti P. Correlated and gauge invariant calculations of nuclear magnetic shielding constants using the continuous transformation of the origin of the current density approach. *J Chem Phys* 2003, 118:6830–6845.
70. Sałek P, Vahtras O, Helgaker T, Ågren H. Density-functional theory of linear and nonlinear time-dependent molecular properties. *J Chem Phys* 2002, 117:9630–9645.
71. Packer MJ, Dalskov EK, Enevoldsen T, Jensen HJAa, Oddershede J. A new implementation of the second-order polarization propagator approximation (SOPPA): the excitation spectra of benzene and naphthalene. *J Chem Phys* 1996, 105: 5886–5900 .

 © 2013 John Wiley & Sons, Ltd.

72. Helgaker T, Coriani S, Jørgensen P, Kristensen K, Olsen J, Ruud K. Recent advances in wave function-based methods of molecular-property calculations. *Chem Rev* 2012, 112:543–631.
73. Hettema H, Jensen HJAa, Jørgensen P, Olsen J. Quadratic response functions for a multiconfigurational self-consistent field wave-function. *J Chem Phys* 1992, 97:1174–1190.
74. Luo Y, Vahtras O, Ågren H, Jørgensen P. Multiconfigurational quadratic response theory calculations of two-photon electronic transition probabilities of H_2O. *Chem Phys Lett* 1993, 204:587–594.
75. Sałek P, Vahtras O, Guo J, Luo Y, Helgaker T, Ågren H. Calculations of two-photon absorption cross sections by means of density-functional theory. *Chem Phys Lett* 2003, 374:446–452.
76. Jansík B, Rizzo A, Ågren H. Response theory calculations of two-photon circular dichroism. *Chem Phys Lett* 2005, 414:461–467.
77. Tunell I, Rinkevicius Z, Vahtras O, Sałek P, Helgaker T, Ågren H. Density functional theory of nonlinear triplet response properties with applications to phosphorescence. *J Chem Phys* 2003, 119:11024–11034.
78. Norman P, Jonsson D, Vahtras O, Ågren H. Nonlinear electric and magnetic properties obtained from cubic response functions in the random phase approximation. *Chem Phys* 1996, 203, 23–42.
79. Jonsson D, Norman P, Ågren H. Cubic response functions in the multiconfiguration self-consistent field approximation. *J Chem Phys* 1996, 105:6401–6419.
80. Jansík B, Sałek P, Jonsson D, Vahtras O, Ågren H. Cubic response functions in time-dependent density functional theory. *J Chem Phys* 2005, 122:054107.
81. Cronstrand P, Jansík B, Jonsson D, Luo Y, Ågren H. Density functional theory calculations of three-photon absorption. *J Chem Phys* 2004, 121:9239–9246.
82. Jonsson D, Norman P, Luo Y, Ågren H. Response theory for static and dynamic polarizabilities of excited states. *J Chem Phys* 1996, 105:581–587.
83. Rizzo A, Ågren H. *Ab initio* study of circular intensity difference in electric-field second harmonic generation of chiral natural amino acids. *Phys Chem Chem Phys* 2013, 15:1198–1207.
84. Halkier A, Koch H, Christiansen O, Jørgensen P, Helgaker T. First-order one-electron properties in the integral-direct coupled cluster singles and doubles model. *J Chem Phys* 1997, 107:849–866.
85. Christiansen O, Koch H, Halkier A, Jørgensen P, Helgaker T, Sánchez de Merás A. Large-scale calculations of excitation energies in coupled cluster theory: the singlet excited states of benzene. *J Chem Phys* 1996, 105:6921–6939.
86. Christiansen O, Halkier A, Koch H, Jørgensen P, Helgaker T. Integral-direct coupled cluster calculations of frequency-dependent polarizabilities, transition probabilities and excited-state properties. *J Chem Phys* 1998, 108:2801–2816.
87. Hättig C, Christiansen O, Koch H, Jørgensen P. Frequency-dependent first hyperpolarizabilities using coupled cluster quadratic response theory. *Chem Phys Lett* 1997, 269:428–434.
88. Hättig C, Christiansen O, Jørgensen P. Frequency-dependent second hyperpolarizabilities using coupled cluster cubic response theory. *Chem Phys Lett* 1998, 282:139–146.
89. Hättig C, Christiansen O, Jørgensen P. Coupled cluster response calculations of two-photon transition probability rate constants for helium, neon and argon. *J Chem Phys* 1998, 108:8355–8359.
90. Hald K, Jørgensen P, Christiansen O, Koch H. Implementation of singlet and triplet excitation energies in coupled cluster theory with approximate triples corrections. *J Chem Phys* 2002, 116:5963–5970.
91. Hättig C, Christiansen O, Coriani S, Jørgensen P. Static and frequency-dependent polarizabilities of excited singlet states using coupled cluster response theory. *J Chem Phys* 1994, 109:9237–9243.
92. Ågren H, Carravetta V, Vahtras O, Pettersson LGM. Direct, atomic orbital, static exchange calculations of photoabsorption spectra of large molecules and clusters. *Chem Phys Lett* 1994, 222: 75–81.
93. Ågren H, Jensen HJAa. An efficient method for calculation of generalized overlap amplitudes for core photoelectron shake-up spectra. *Chem Phys Lett* 1987, 137:431–436.
94. Luo Y, Vahtras O, Gel'mukhanov F, Ågren H. Theory of natural circular dichroism in X-ray Raman scattering from molecules. *Phys Rev A* 1997, 55:2716–2722.
95. Vahtras O, Ågren H, Carravetta V. Natural circular dichroism in non-resonant X-ray emission. *J Phys B* 1997, 30:1493–1501.
96. Norman P, Bishop DM, Jensen HJAa, Oddershede J. Nonlinear response theory with relaxation: the first-order hyperpolarizability. *J Chem Phys* 2005, 123:194103.
97. Norman P, Bishop DM, Jensen HJAa, Oddershede J. Near-resonant absorption in the time-dependent self-consistent field and multiconfigurational self-consistent field approximations. *J Chem Phys* 2001, 115:10323–10334.
98. Coriani S, Christiansen O, Fransson T, Norman P. Coupled-cluster response theory for near-edge X-ray-absorption fine structure of atoms and molecules. *Phys Rev A* 2012, 85:022507.
99. Coriani S, Fransson T, Christiansen O, Norman P. Asymmetric-Lanczos-chain-driven implementation of electronic resonance convergent coupled cluster linear response theory. *J Chem Theory Comput* 2012, 8:1616–1628.

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100. Kauczor J, Jørgensen P, Norman P. On the efficiency of algorithms for solving Hartree–Fock and Kohn–Sham response equations. *J Chem Theory Comput* 2011, 7:1610–1630.
101. Jiemchooroj A, Norman P. Electronic circular dichroism spectra from the complex polarization propagator. *J Chem Phys* 2007, 126: 134102.
102. Mohammed A, Ågren H, Norman P. Resonance enhanced Raman scattering from the complex electric-dipole polarizability: a theoretical study on N_2. *Chem Phys Lett* 2009, 468:119–123.
103. Solheim H, Ruud K, Coriani S, Norman P. Complex polarization propagator calculations of magnetic circular dichroism spectra. *J Chem Phys* 2008, 128:094103.
104. Ekström U, Norman P, Carravetta V, Ågren H. Polarization propagator for X-ray spectra. *Phys Rev Lett* 2006, 97:143001.
105. Ahrén M, Selegård L, Söderlind F, Linares M, Kauczor J, Norman P, Käll P-O, Uvdal K. A simple polyol-free synthesis route to Gd_2O_3 nanoparticles for MRI applications: an experimental and theoretical study. *J Nanopart Res* 2012, 14:1006.
106. Mikkelsen KV, Ågren H, Jensen HJAa, Helgaker T. A multiconfigurational self-consistent reaction-field method. *J Chem Phys* 1988, 89:3086–3095.
107. Mikkelsen KV, Cesar A, Ågren H, Jensen HJAa. Multiconfigurational self-consistent reaction-field theory for nonequilibrium solvation. *J Chem Phys* 1995, 103: 9010–9023.
108. Christiansen O, Mikkelsen KV. A coupled-cluster solvent reaction field method. *J Chem Phys* 1999, 110:1365–1375.
109. Mikkelsen KV, Jørgensen P, Jensen HJAa. A multiconfiguration self consistent reaction field response method. *J Chem Phys* 1994, 100:6597–6607.
110. Mikkelsen KV, Sylvester-Hvid KO. A molecular response method for solvated molecules in nonequlibrium solvation. *J Phys Chem* 1996, 100:9116–9126.
111. Fernández B, Christensen O, Bludsky O, Jørgensen P, Mikkelsen KV. Theory of hyperfine coupling constants of solvated molecules: applications involving methyl and ClO_2 radicals in different solvents. *J Chem Phys* 1996, 104:629–635.
112. Mikkelsen KV, Jørgensen P, Ruud K, Helgaker T. A multipole reaction-field model for gauge-origin independent magnetic properties of solvated molecules. *J Chem Phys* 1997, 106:1170–1180.
113. Sylvester-Hvid KO, Mikkelsen KV, Jonsson D, Norman P, Ågren H. Nonlinear optical response of molecules in a nonequilibrium solvation model. *J Chem Phys* 1998, 109:5576–5584.
114. Christiansen O, Mikkelsen KV. Coupled cluster response theory for solvated molecules in equilibrium and nonequilibrium solvation. *J Chem Phys* 1999, 110:8348–8360.
115. Cammi R, Frediani L, Mennucci B, Tomasi J, Ruud K, Mikkelsen KV. A second-order, quadratically convergent multiconfigurational self-consistent field polarizable continuum model for equilibrium and nonequilibrium solvation. *J Chem Phys* 2002, 117:13–26.
116. Cammi R, Frediani L, Mennucci B, Ruud K. Multiconfigurational self-consistent field linear response for the polarizable continuum model: theory and application to ground and excited-state polarizabilities of para-nitroaniline in solution. *J Chem Phys* 2003, 119:5818–5827.
117. Frediani L, Ågren H, Ferrighi L, Ruud K. Second-harmonic generation of solvated molecules using multiconfigurational self-consistent-field quadratic response theory and the polarizable continuum model. *J Chem Phys* 2005, 123:144117.
118. Ferrighi L, Frediani L, Ruud K. Degenerate four-wave mixing in solution by cubic response theory and the polarizable continuum model. *J Phys Chem B* 2007, 111:8965–8973.
119. Kongsted J, Osted A, Mikkelsen KV, Christiansen O. The QM/MM approach for wavefunctions, energies and response functions within self-consistent field and coupled cluster theories. *Mol Phys* 2002, 100:1813–1828.
120. Osted A, Kongsted J, Mikkelsen KV, Christiansen O. A CC2 dielectric continuum model and a CC2 molecular mechanics model. *Mol Phys* 2003, 101:2055–2071.
121. Kongsted J, Osted A, Mikkelsen KV, Christiansen O. Linear response functions for coupled cluster/molecular mechanics including polarization interactions. *J Chem Phys* 2003, 118:1620–1633.
122. Olsen JM, Aidas K, Kongsted J. Excited states in solution through polarizable embedding. *J Chem Theory Comput* 2010, 6:3721–3734.
123. Olsen JMH, Kongsted J. Molecular properties through polarizable embedding. *Adv Quantum Chem* 2011, 61:107–143.
124. Eriksen JJ, Sauer SPA, Mikkelsen KV, Jensen HJAa, Kongsted J. On the importance of excited state dynamic response electron correlation in polarizable embedding methods. *J Comput Chem* 2012, 33:2012–2022.
125. Sneskov K, Schwabe T, Kongsted J, Christiansen O. The polarizable embedding coupled cluster method. *J Chem Phys* 2012, 134:104108–104123.
126. Sałek P, Høst S, Thøgersen L, Jørgensen P, Manninen P, Olsen J, Jansík B, Reine S, Pawłowski F, Tellgren E, Helgaker T, Coriani S. Linear-scaling implementation of molecular electronic self-consistent field theory. *J Chem Phys* 2007, 126:114110.
127. Høst S, Olsen J, Jansík B, Thøgersen L, Jørgensen P, Helgaker T. The augmented Roothaan–Hall method for optimizing Hartree–Fock and Kohn–Sham density matrices. *J Chem Phys* 2008, 129:124106.

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128. Jansík B, Høst S, Johansson MP, Olsen J, Jørgensen P, Helgaker T. A stepwise atomic, valence-molecular, and full-molecular optimisation of the Hartree–Fock/Kohn–Sham energy. *Phys Chem Chem Phys* 2009, 11:5805–5813.
129. White CA, Johnson BG, Gill PMW, Head-Gordon M. The continuous fast multipole method. *Chem Phys Lett* 1994 230:8–16.
130. Watson MA, Sałek P, Macak P, Helgaker T. Linear-scaling formation of Kohn–Sham Hamiltonian: application to the calculation of excitation energies and polarizabilities of large molecular systems. *J Chem Phys* 2004, 121:2915–2931.
131. Ochsenfeld C, White CA, Head-Gordon M. Linear and sublinear scaling formation of Hartree–Fock-type exchange matrices. *J Chem Phys* 1998, 109:1663–1669.
132. Reine S, Tellgren E, Krapp A, Kjærgaard T, Helgaker T, Jansík B, Høst S, Sałek P: Variational and robust density fitting of four-center two-electron integrals in local metrics. *J Chem Phys* 2008, 129:104101.
133. Coriani S, Høst S, Jansík B, Thøgersen L, Olsen J, Jørgensen P, Reine S, Pawłowski F, Helgaker T, Sałek P. Linear-scaling implementation of molecular response theory in self-consistent field electronic-structure theory. *J Chem Phys* 2007, 126:154108.
134. Thorvaldsen AJ, Ruud K, Kristensen K, Jørgensen P, Coriani S. A density matrix-based quasi-energy formulation of the Kohn–Sham density functional response theory using perturbation- and time-dependent basis sets. *J Chem Phys* 2008, 129: 214108.
135. 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 Comp* 2009, 5:1997–2020.
136. Kjærgaard T, Kristensen K, Kauczor J, Jørgensen P, Coriani S, Thorvaldsen AJ. Comparison of standard and damped response formulations of magnetic circular dichroism. *J Chem Phys* 2011, 135: 024112
137. Kristensen K, Kauczor J, Kjærgaard T, Jørgensen P. Quasi-energy formulation of damped response theory. *J Chem Phys* 2009, 131:044112.
138. Jansík B, Høst S, Kristensen K, Jørgensen P. Local orbitals by minimizing powers of the orbital variance. *J Chem Phys* 2011, 134:194104.
139. Høyvik I-M, Jansík B, Jørgensen P. Trust region minimization of orbital localization functions. *J Chem Theory Comput* 2012, 8:3137–3146.
140. Ziólkowski M, Jansík B, Kjærgaard T, Jørgensen P. Linear scaling coupled-cluster method with correlation energy based error control. *J Chem Phys* 2010, 133:014107.
141. Kristensen K, Jørgensen P, Jansík B, Kjærgaard T, Reine S. Molecular gradient for second-order Møller–Plesset perturbation theory using the Divide-Expand-Consolidate (DEC) scheme. *J Chem Phys* 2012, 137:114102.
142. Kristensen K, Høyvik I-M, Jansík B, Jørgensen P, Kjærgaard T, Reine S, Jakowski J. MP2 energy and density for large molecular systems with internal error control using the Divide-Expand-Consolidate scheme. *Phys Chem Chem Phys* 2012, 14:15706–15714.
143. Helgaker T, Taylor PR, *HERMIT, A Molecular Integral Code*. University of Oslo, Oslo, Norway; 1986.
144. Helgaker T, Jensen HJAa, Jørgensen, P, Olsen, J, Taylor PR. *ABACUS, A Molecular Property Code*. University of Oslo, Oslo, Norway; 1986.
145. Jørgensen P, Jensen HJAa, Olsen J. *RESPONS, A Molecular Response Code*. Aarhus University, Aarhus, Denmark; 1988.
146. Koch H, Sánchez de Merás A, Pedersen TB. Reduced scaling in electronic structure calculations using Cholesky decompositions. *J Chem Phys* 2003, 118:9481–9484.
147. Peach MJG, Helgaker T, Salek P, Keal TW, Lutnæs OB, Tozer DJ, Handy NC. Assessment of a Coulomb-attenuated exchange–correlation energy functional. *Phys Chem Chem Phys* 2006, 8:558–562.
148. Peach MJG, Benfield P, Helgaker T, Tozer DJ. Excitation energies in density functional theory: an evaluation and a diagnostic test. *J Chem Phys* 2008, 128:044118.
149. Bak KL, Koch H, Oddershede J, Christiansen O, Sauer SPA. Atomic integral driven second order polarization propagator calculations of the excitation spectra of naphthalene and anthracene. *J Chem Phys* 2000, 112:4173–4185.
150. Christiansen O, Bak KL, Koch H, Sauer SPA. A second-order doubles correction to excitation energies in the random phase approximation. *Chem Phys Lett* 1998, 284:47–55.
151. Vahtras O, Rinkevicius Z. General excitations in time-dependent density functional theory. *J Chem Phys* 2007, 126:114101.
152. Rinkevicius Z, Vahtras O, Ågren H. Spin-flip time dependent density-functional theory applied to excited states with single, double, or mixed electron excitation character. *J Chem Phys* 2010, 133:114104.
153. Norman P, Jonsson D, Ågren H, Dahle P, Ruud K, Helgaker T, Koch H. Efficient parallel implementation of response theory: calculations of the second hyperpolarizability of polyacenes. *Chem Phys Lett* 1996 253:1–7.
154. Steindal AH, Olsen JMH, Frediani L, Kongsted J, Ruud K. Parallelization of the polarizable embedding scheme for higher-order response functions. *Mol Phys* 2012, 110:2579–2586.

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155. Fossgård E, Ruud K. Superlinear scaling in master-slave quantum chemical calculations using in-core storage of two-electron integrals. *J Comput Chem* 2006, 27:326–333.

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