Software Focus

Turbomole

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Turbomole is a highly optimized software package for large-scale quantum chemical simulations of molecules, clusters, and periodic solids. Turbomole uses Gaussian basis sets and specializes on predictive electronic structure methods with excellent cost to performance characteristics, such as (time-dependent) density functional theory (TDDFT), second-order Møller–Plesset theory, and explicitly correlated coupled cluster (CC) methods. These methods are combined with ultraefficient and numerically stable algorithms such as integral-direct and Laplace transform methods, resolution-of-the-identity, pair natural orbitals, fast multipole, and low-order scaling techniques. Apart from energies and structures, a variety of optical, electric, and magnetic properties are accessible from analytical energy derivatives for electronic ground and excited states. Recent additions include post-Kohn–Sham calculations within the random phase approximation, periodic calculations, spin–orbit couplings, explicitly correlated CC singles doubles and perturbative triples methods, CC singles doubles excitation energies, and nonadiabatic molecular dynamics simulations using TDDFT. A dedicated graphical user interface and a user support network are also available. © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

The aim of the Turbomole project is to provide highly efficient and stable computational tools for large-scale quantum chemical simulations of molecules, clusters, and, more recently, surfaces and periodic solids. Typical Turbomole applications include structure optimizations and transition-state searches in ground and electronically excited states, calculations of energies and thermodynamic functions, optical, electric, and magnetic properties, and molecular dynamics simulations. Solvation effects may be included using the conductor-like screening model (COSMO). Turbomole is meant to be a production rather than an experimental code, and focuses on widely applicable electronic structure methods with excellent cost-performance characteristics such as density functional theory (DFT), second-order Møller–Plesset (MP2) and coupled cluster (CC) theory. Low-order scaling is achieved by integral direct algorithms, Laplace-transform methods, and by exploiting sparsity, whereas resolution-of-the-identity (RI) methods and support of non-Abelian point group symmetry provide substantial additional acceleration. Turbomole's integral evaluation and quadrature schemes are optimized for segmented contracted Gaussian basis sets that are available for all elements. Turbomole is most efficient on medium-size compute clusters, but the latest additions increasingly support massively parallel architectures.

Turbomole was initiated in 1987 and developed into a full-fledged program system under the supervision of Reinhart Ahlrichs.[1] Twenty years later, the authors of this review founded Turbomole GmbH to

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facilitate the continued improvement and broad dissemination of the Turbomole software. While most of the source code is proprietary, Turbomole GmbH grants source code licenses based on code development proposals. Turbomole is distributed through COSMO*logic* GmbH & Co. KG, and a variety of licenses for all major operating systems are commercially available. Besides direct user support, COSMO*logic* provides a free graphical user interface for Turbomole; many other programs can also be interfaced to Turbomole. Turbomole's user base increasingly includes nonspecialists and spans academic and educational institutions, government, and industry.

This Software Focus highlights some of Turbomole's most distinctive and recent features. A comprehensive list of Turbomole's functionalities and original references are available in the users' manual (see Turbomole webpage under Further Reading/Resources). Release notes for the latest version are posted on the Turbomole webpage.

ELECTRONIC GROUND STATES

Highly Efficient Hybrid DFT, MP2, and RPA Methods

Electron Repulsion Integrals

DFT calculations are the mainstay of present-day computational quantum chemistry. The evaluation of two-electron four-center electron repulsion integrals (ERIs) is rate-determining in most DFT, Hartree–Fock (HF), and even many MP2 calculations. Turbomole's ERI processing is based on the Obara–Saika algorithm augmented by hand-coded subroutines for low angular momentum ERIs. Timings scale quadratically with the system size N for large molecules since the evaluation of negligible terms is avoided by screening. The high efficiency of Turbomole's direct HF implementation is illustrated for the low and high symmetry arsenic clusters[2] As_{90} (C_2) and As_{144} (D_{6d}) in Table 1.

TABLE 1 | Wall Times (Minutes) for Single-Point Energy Calculations Using def2-TZVPP Basis Sets

	As_{90}	As_{144}
HF (dscf)	496	126
RI-*J*-HF (ridft)	94	25
MARI-*J*-BP86 (ridft)	16	10
RI-MP2 (ricc2)	2862	2341

C_2 symmetry was imposed for As_{90} and D_{6d} for As_{144}. The structures were taken from Ref 2. Twelve cores on an Intel dual hex-core X5650 (2.67 GHz) were used. The HF calculations were started using converged BP86 molecular orbitals. The HF (dscf) calculations were done in integral direct mode, whereas the RI-*J* calculations used 10 GB of memory for integral storage. The DFT calculations employed quadrature grids of size m4 and were started from an extended Hückel guess. The ricc2 calculations used a frozen Ar core and 20 GB of memory; the timings are for the MP2 correlation energy only.

RI-J and MARI-J Approximations

Further speedup results from separating the calculation of the Coulomb (J) and exchange (K) contributions to the energy and Fock matrix. This is particularly useful for non-hybrid DFT, but significant speedups are also observed in RI-*J* HF and hybrid DFT calculations due to more efficient ERI screening and processing for exchange only, see Table 1. Because J is fully specified by the total molecular electron density ρ-a one-electron quantity without too much structure-one may approximate or 'fit' ρ by an expansion in an auxiliary basis set. This method has been termed RI-*J* approximation. The Karlsruhe group was the first to optimize auxiliary basis sets and assess errors introduced by the RI-*J* approximation systematically. RI-*J* requires two- and three-center integrals only, which is exploited by fast integral routines developed for this special case.[3] RI-*J* scales as $O(N^2)$, but timings for J are typically 40 times less than for the conventional procedure. RI-*J* errors are usually below 0.05 mHartree/atom, which is much less than typical errors caused by finite atomic orbital (AO) basis sets used to represent molecular orbitals. Karlsruhe auxiliary basis sets for RI-*J* are available throughout the periodic table and for many popular AO basis sets.[4]

The multipole-accelerated RI-*J* (MARI-*J*) procedure splits Coulomb interactions into a near- and a far-field contribution and evaluates the latter with the help of the multipole expansion.[5] This leads to considerable savings, especially for larger molecules: The scaling exponent is reduced to about 1.5 for space-filling systems such as graphitic sheets, zeolite fragments or fractions of diamond, whereas the loss of accuracy is negligible. Using MARI-*J*, a non-hybrid DFT single-point energy for systems in the size range of As_{90} and As_{144} takes a few minutes on 12 cores using polarized triple zeta basis sets, see Table 1.

Exchange-Correlation Energy and Potential

Turbomole's quadrature algorithm[6] for the exchange-correlation (XC) energy and potential partitions the integrand into atom-centered partitions using Becke's method. For the resulting atomic quadrature problem, spherical Lebedev grids and radial Gauss–Chebychev grids with atom-optimized mapping functions are used. Seven predefined default grids along with special grids for diffuse densities and reference purposes are available. Linear scaling is achieved by ordering the

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grid into localized 'batches' and exploiting the locality of the Gaussian basis functions. Platform-optimized basic linear algebra subroutines, recursive construction of the density and the XC potential on the grid over several iterations, and multigrid methods lead to further substantial speed-ups. Turbomole supports the most common semi-local functionals with the local spin-density approximation, generalized gradient approximation (GGA), meta-GGA, as well as hybrid functionals containing a fraction of HF exchange.

RI for Exchange and MP2

The RI technique is also effective in the treatment of the exchange contribution to the HF or the (hybrid) DFT energy. This RI-*JK* method requires larger auxiliary basis sets than RI-*J* and the gains in speed are less spectacular. RI-*JK* is mainly useful for larger basis sets and smaller molecules. For instance, a conventional HF single-point energy calculation of tris(2-phenylpyridine)iridium using QZVPP basis sets takes 174 h on a single 2.7 GHz Intel Xeon CPU core, but only 26 h when RI-*JK* is enabled.

The RI-MP2 method uses RI to speed up the evaluation of the MP2 energy and its gradient.[7] The necessary auxiliary bases are available across the periodic table for many common AO basis sets.[8] RI-MP2 timings for As_{90} and As_{144} are reported in Table 1.

Accurate Density Functional Calculations using the Random Phase Approximation

The random phase approximation (RPA) is a parameter-free density functional alternative to MP2 that can be applied to small-gap systems. RPA includes long-range dispersion interactions and may be used to validate semi-local DFT results.[9] Turbomole's RI-RPA implementation scales as $O(N^4\log(N))$ and has been applied to systems with well over 100 atoms.[10] The analytical RI-RPA gradient, which will be first released in Turbomole V6.6, allows geometry optimizations of weakly bound complexes and crowded systems where most other density functionals fail.

Surfaces and Solids

Periodic Electrostatic Embedded Cluster Method

The Periodic Electrostatic Embedded Cluster Method (PEECM) may be applied within combined quantum mechanics/molecular mechanics (QM/MM) schemes for efficient evaluation of electrostatic interactions between the QM part and an infinite periodic array of point charges (PC).[11] It uses multipole expansions to calculate the Madelung potential and is able to treat periodic PC arrays of any dimensionality (i.e., three-, two-, and one-dimensional periodicity). Figure 1 illustrates the use of PEECM for modeling electron localization in defective ceria films.[12]

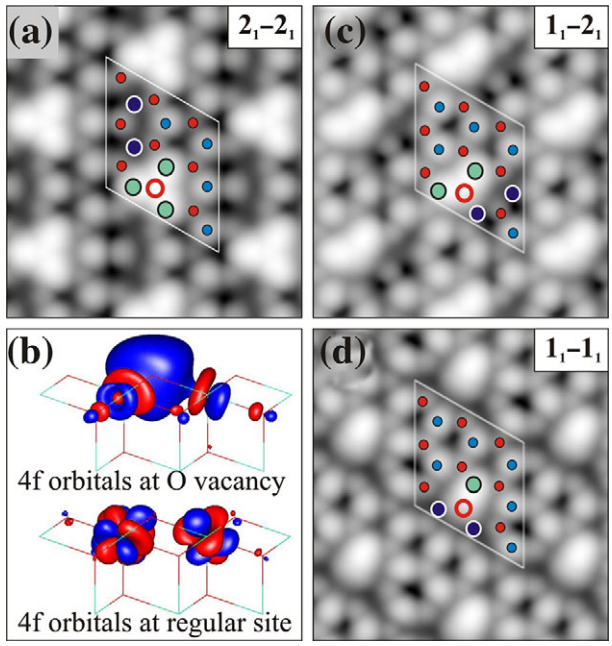


FIGURE 1 | DFT simulations of empty-state STM images (0–2 eV) of defective ceria films. Small blue dots denote Ce^{4+} ions, red dots O^{2-} ions, and the red circle the O vacancy. While Ce^{3+} ions (large blue circles) are nearly invisible, Ce^{4+} ions next to the O defect appear brighter. This results in different patterns depending on the number of Ce^{4+} ions around the defect. The origin of the contrast is the larger expansion of the Ce^{4+} 4*f* orbitals in the presence of the vacancy (b). Reprinted with permission from Ref 12. Copyright 2011 by the American Physical Society. Online abstract: http://prl.aps.org/abstract/PRL/v106/i24/e246801.

Periodic DFT Calculations

An extension of the density functional methods available within Turbomole to periodic systems such as polymers, surfaces, interfaces, and bulk solids is presently under development. The main features of this new implementation are sparse storage of real space integrals and density matrices as well as the use of a hierarchical approach for numerical integration of XC terms.[13] The key component is a new formulation of RI approximation for the Coulomb term, which treats molecular and periodic systems of any dimensionality on an equal footing.[14]

Relativistic Effects

Effective core potentials (ECPs) provide a simple and efficient way to account for scalar relativistic

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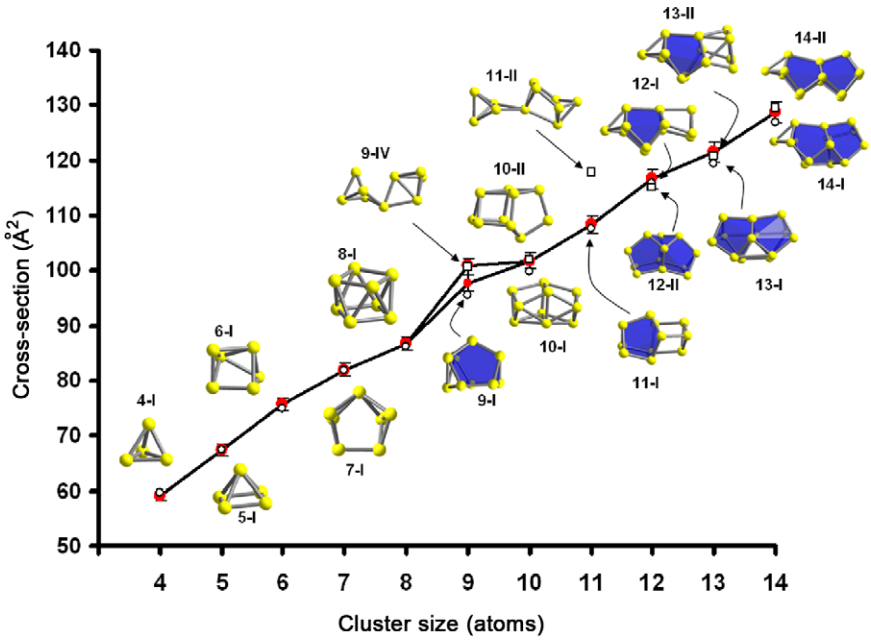


FIGURE 2 | Collision cross-sections of bismuth cluster cations as a function of cluster size. Experimental electron diffraction results are shown as full circles with error bars. Computed global minimum structures are labeled by open circles; other low-energy minima are denoted by open squares. The computed structures were generated by two-component DFT calculations. Reproduced with permission from Ref 16. Copyright 2012, American Institute of Physics.

effects in electronic structure calculations. Scalar relativistic ECPs are available for all Turbomole functionalities except nuclear magnetic shielding calculations. Turbomole's recommended ECPs for Rb-Rn are the Dirac–Fock ECPs by the Stuttgart–Köln group. For these ECPs, segmented contracted polarized basis sets of double to quadruple zeta valence quality were published recently (dhf-XVP, X = S,TZ,QZ).[15] For the lanthanides, Wood-Boring ECPs are available along with optimized segmented contracted basis sets.

Turbomole is one of the few codes supporting spin–orbit coupling (SOC) in self-consistent calculations. SOC effects can be important even for ground-state properties, as demonstrated in a recent study of bismuth cluster cations,[16] see Figure 2.

Self-consistent SOC coupling requires two-component, complex one-particle wave functions ('spinors'). The higher dimensionality of the two-component formalism increases computational cost compared with the one-component case. Nevertheless, two-component (nonhybrid) DFT calculations with several thousand basis functions (several hundred atoms) are routinely feasible with Turbomole.[17] Also available are two-component analytic geometry gradients at the HF and DFT levels as well as two-component MP2 energies.

BOX 1: MOLECULAR CLUSTERS

Finding the global minimum structures of molecular clusters is challenging because of the steeply increasing number of low-energy isomers with the cluster size. The combination of genetic algorithm (GA)-driven global optimization with trapped ion electron diffraction experiments is a reliable method to determine the structures of charged clusters in the gas phase, as illustrated for bismuth cluster cations in Figure 2. The cross-sections of minimum structures obtained with SOC agree much better with the experiment than those obtained without it.

Explicitly Correlated Wavefunction Methods

Overview

Correlated wavefunction methods require very large AO basis sets for accurate predictions of energies close to the limit of a complete basis set. This is due to the painfully slow convergence of the correlation energy with the size of the AO basis: Errors in molecular correlation energies vanish as n^{-1}, where n is the size of the AO basis, even with basis sets designed and optimized especially for describing electron correlation effects. Fortunately, this slow convergence can be

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TABLE 2 | CCSD(F12) Binding Energies (D_e in kJ mol^{-1}) of the Lithium—Thiophene Complex

Basis[1]	Basis-set size	Hartree–Fock (UHF)	CABS correction	CCSD(F12) correlation ($\gamma = 1.1\ a_0^{-1}$)	Total	Wall clock time[2] (min)
cc-pVDZ-F12	229	−24.76	−1.59	59.46	33.11	20/7
cc-pVTZ-F12	408	−26.31	0.07	62.82	36.58	134/39
cc-pVQZ-F12[3]	676	−26.29	0.10	63.30	37.11	649/274

The CCSD(F12) correlation energy converges rapidly to the basis set limit. The Hartree–Fock energy in the cc-pVDZ-F12 basis is much improved by the CABS singles term.
[1] cc-pCVXZ-F12 (X = D, T, Q) for Li while correlating its 1*s* orbital; counterpoise corrected.
[2] Time on 6 cores of an Intel dual hex-core X5650 (2.67 GHz) for MP2-F12/single CCSD(F12) iteration in C_1 symmetry.
[3] From Ref 23.

dramatically accelerated using explicitly correlated wavefunctions. In Turbomole, explicitly correlated wavefunction methods are available at the levels of MP2 theory (including spin-component scaled variants) as well as coupled-cluster theory with singles and doubles (CCSD). The corresponding explicitly correlated methods are known as (SCS-) MP2-F12[18] and CCSD-F12,[19] as they include two-electron basis functions of the interelectronic coordinate, $f(r_{12})$. In Turbomole, these functions are Slater-type geminals of the form $f(r_{12}) = \exp(-\gamma\ r_{12})$, which are expanded in a few Gaussian-type geminals. The explicitly correlated methods (or F12 methods) are available in Turbomole for the computation of single-point energies using either an unrestricted HF (UHF) or a restricted (open-shell) HF reference determinant [R(O)HF]. Nuclear gradients are available at the MP2-F12 level within the 2*A approximation.[20] A perturbative, noniterative correction for connected triple excitations is added to the energy at the CCSD(T)-F12 level which is also available in Turbomole.

MP2-F12 Theory

The MP2-F12 method has been implemented using RI methods and parallelized for shared-memory architectures. Molecules as large as prednisone (52 atoms) or methotrexate (55 atoms) using basis sets as large as aug-cc-pVQZ (3276/3652 orbitals) are well within reach for our implementation. The method is available in two approximations (A and B). It is recommended to use the fixed-amplitudes ansatz (also denoted as *sp*- or rational generator ansatz) for large molecular systems. Usually, the total energy is supplemented by an energy correction that is obtained by allowing for single excitations into the complementary auxiliary basis set (CABS), which is used for certain three- and four-electron integrals occurring in F12 theory. This correction is known as CABS singles term. Canonical as well as localized orbitals may be used. Very recently, a *local* explicitly correlated second-order (and third-order) Møller–Plesset perturbation theory approach was implemented using pair natural orbitals.[21] In addition, the approximate MP3- and MP4-F12 models MP3(F12) and MP4(F12) will be released in Turbomole V6.5.

CCSD(T)-F12 Theory

Approximate CCSD(T)-F12 models such as CCSD(T)(F12) or CCSD(T)(F12*) may be used to obtain highly accurate CCSD(T) energies close to the limit of a complete basis set. For example, new accurate reference atomization energies (AEs) for the G2/97 test set (which comprises 148 molecules) were recently computed at the CCSD(T)(F12)/cc-pVQZ-F12 level.[22] By including corrections for excitations beyond CCSD(T) as well as for core–core- and core–valence correlation effects, very accurate values of the nonrelativistic Born–Oppenheimer AEs were obtained. With the current version of Turbomole, CCSD(F12)/cc-pVQZ-F12 calculations can be performed routinely on systems such as the lithium–thiophene complex, see Table 2.[23]

ELECTRONIC EXCITED STATES AND TIME-DEPENDENT RESPONSE

Time-Dependent DFT

Vertical Excitations and Response Properties

Electronic vertical excitation energies, transition moments, oscillator and rotatory strengths of closed and open-shell systems are efficiently computed using time-dependent HF and adiabatic TDDFT. At the core of Turbomole's TDDFT functionality is a block Davidson-type iterative solver that can treat hundreds of excitations simultaneously. This implementation has been used to simulate electronic excitation and circular dichroism spectra of molecules with 100–1000 atoms over a range of several eV.[24] Similarly, response properties such as polarizabilities and optical rotations may be computed at many different frequencies in one single calculation. Oscillator strengths of spin-forbidden transitions and spin–orbit

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splitting of excitation energies are accessible through two-component SOC calculations using ECPs.

Analytical Excited-State Gradients, Nonadiabatic Couplings, and Raman Intensities

Turbomole's analytical TDDFT gradient implementation[25] makes it possible to optimize the structures of electronically excited states with similar efficiency as ground states. This may be used, e.g., to investigate fluorescence spectra and fluorescence lifetimes. Excited-state vibrational properties are available through finite differences of analytical gradients. First-order nonadiabatic couplings between the ground and an excited state can be evaluated during an excited-state gradient calculation at only ~10% extra cost.[26]

Ground-state frequency-dependent vibrational Raman intensities are very efficiently computed using Turbomole's analytical polarizability gradient.[27] Because the gradient calculation is independent of ground-state analytical second derivatives, large basis sets are affordable even for systems with well over 100 atoms. This implementation works for off- and near-resonant Raman.

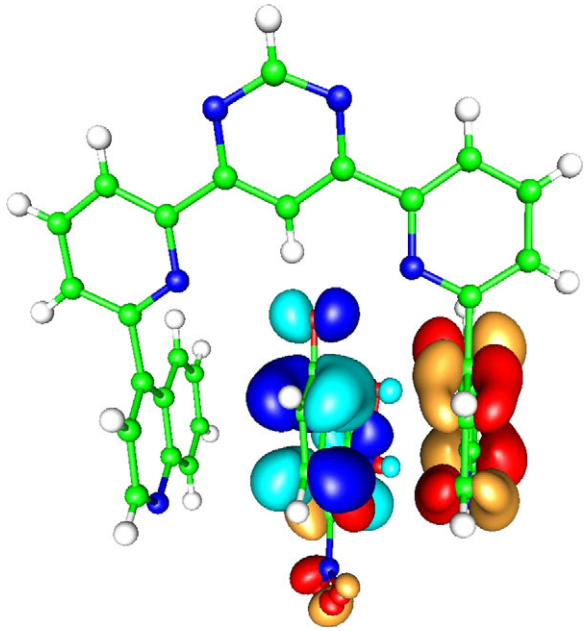


FIGURE 3 | Natural transition orbitals for the 5th excited singlet state in a molecular tweezer complex. As shown by CC2 calculations using cc-pVDZ basis sets, this charge transfer state dominates the two-photon absorption in the UV–vis regime. Reproduced with permission from Ref 30. Copyright 2012, Royal Society of Chemistry.

CC Response Methods

As a wavefunction based alternative to TDDFT, Turbomole provides an implementation of the approximate CCSD model CC2,[28] which uses the RI approximation and builds on efficient techniques originally developed for RI-MP2. Prominent features of the implementation are, besides its computational efficiency, low core memory and disk space demands that scale, respectively, as $O(N^2)$ and $O(N^3)$. Together with a parallelization for distributed memory architectures[29] this makes CC2 excitation energies accessible for molecules with up to ~100 atoms without sacrificing accuracy, for example, by restricting the basis sets. In addition to the CC2 model, the perturbative doubles correction to configuration interaction singles, CIS(D), and the algebraic diagrammatic construction through second-order, ADC(2), are available. Excitation energies within the CCSD model will be released in version V6.5. For single-reference cases, CC2, CIS(D) and ADC(2) are valuable alternatives to TDDFT whenever there is a suspicion that charge-transfer excitations or valence-Rydberg mixing might affect the accuracy of TDDFT by large self-interaction errors. This is illustrated for a charge-transfer excitation in a molecular tweezer complex[30] in Figure 3.

Available functionalities include excitation energies, one-electron properties for ground and excited states, and oscillator and rotatory strengths for transitions from the ground to excited states and transitions between excited states, which can all be combined with UHF or R(O)HF reference determinants, and parallelizations for shared- and distributed memory machines. An outstanding feature of Turbomole is the parallel implementation of analytical gradients[31] for potential energies surfaces of excited states for CC2 and ADC(2).

The MP2, CIS(D), ADC(2), and CC2 methods may be combined with spin-component scaling[32] whose SCS variant yields a substantial improvement of the equilibrium structures of ground and excited states, their vibrational frequencies and 0–0 transition energies without additional computational costs. Using Laplace transform methods, the scaled opposite spin variants have been implemented with $O(N^4)$ scaling while preserving almost the full accuracy of CC2 and ADC(2) for 0–0 transition energies. The reduced computational complexity of SOS methods allows, for example, excited-state geometry optimizations for molecules with more than 150 atoms.[33]

Solvent effects on the excitation energies may be included via COSMO or polarizable embedding (PERI-CC2).[34] Recently, the CC response methods in Turbomole have been extended for the computation of static (MP2, CC2) and frequency-dependent (CC2)

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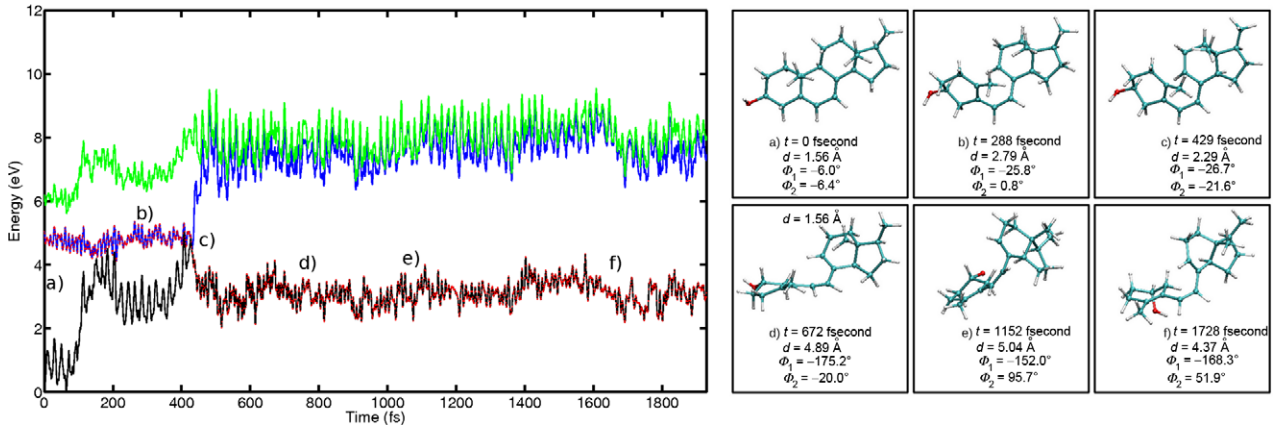


FIGURE 4 | Illustrative PBE0-TDDFT FSSH trajectory showing provitamin D ring opening followed by ground-state isomerization. Black: ground state, blue: S_1, green: S_2; red dots indicate the propagated state. Reproduced with permission from Ref 36. Copyright 2012, Royal Society of Chemistry.

polarizabilities, optical rotatory dispersion (CC2), and two-photon transition intensities.

STRUCTURE OPTIMIZATION AND MOLECULAR DYNAMICS

Local and Global Structure Optimizations

Minima and transition structures may efficiently be optimized using automatically generated internal redundant, user-defined internal and Cartesian coordinates. For locating minima, Turbomole includes many of the modern optimization algorithms and the default optimization method automatically chooses the optimum one. For transition-state optimization, an eigenvector following method has been implemented which combines the quasi-Newton–Raphson, rational function approximation and trust radius image minimization algorithms.

A unique feature of Turbomole is the possibility of searching for global energy minima of molecular structures using most of the electronic structure methods available within the program. The implementation is based on a GA that mimics evolution. The GA starts with a population of randomly generated structures, which are optimized to the nearest local minimum. The evolution from one generation to the next takes place by crossover, where randomly chosen parent structures are combined to yield new children structures. In addition, mutation operations are performed which prevent premature convergence of the GA. Key to the efficiency of the GA implementation is a novel similarity recognition algorithm used to detect basins corresponding to different structural motifs.[35] This implementation has been used in studies of molecular clusters including metals, semiconductors and metal oxides.

BOX 2: VITAMIN D PHOTOCHEMISTRY

The first comprehensive nonadiabatic FSSH simulations of photoexcited Vitamin D derivatives[36] explained the experimentally observed double exponential decay of the S_1 state, as well as quantum yields and mechanisms of the formation of the most important photoproducts, see Figure 4. Using a 51-atom model of Vitamin D, ~400,000 time steps were performed on a medium-size compute cluster, corresponding to a total simulation time of ~0.4 ps. Hybrid functionals were found to be essential for such simulations to avoid spurious intruder states.

Molecular Dynamics Simulations

Turbomole supports *ab initio* molecular dynamics (AIMD) simulations with classical nuclei for virtually all electronic structure methods described above. AIMD is highly useful for locating global minimum structures, probing reaction mechanisms, and calculating ensemble properties at finite temperature. Simulations may be performed in the microcanonical (NVE) and canonical (NVT) ensembles.

In combination with Tully's Fewest Switches Surface Hopping (FSSH) algorithm, TDDFT analytical forces and nonadiabatic couplings may be combined in highly efficient excited-state nonadiabatic molecular dynamics simulations that have recently become possible with Turbomole,[36] see Figure 4.

CONCLUSION

Turbomole continues to play an important role in computational quantum chemistry by providing

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highly efficient and stable implementations in many important areas, such as integral-direct algorithms, RI methods, efficient DFT and TDDFT calculations, RI-CC2 methods, and F12-CC methods. With an increasing number of active Turbomole developers and a fee system supporting code maintenance, user support, and long-term stability, Turbomole is well positioned for the future. A major ongoing effort is the continued improvement of Turbomole's user-friendliness, as the majority of Turbomole users no longer are method developers or even theoretical chemists. Important new directions include nonadiabatic molecular dynamics, ultraefficient higher-order CC methods, new density functionals, and periodic calculations.

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FURTHER READING/RESOURCES

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