Supplementary Material for TURBOMOLE: Modular Program Suite for ab initio Quantum-Chemical and Condensed-Matter Simulations

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I. HISTORY

Initiated by Marco Häser in 1987, TURBOMOLE was developed into a full-fledged program suite[1] under the direction of Reinhart Ahlrichs, whose vision was a quantum chemistry program for cutting-edge applications with industrial level standards for robustness and efficiency. Thus, Ahlrichs coined the motto "tools not toys", distinguishing TURBOMOLE from more experimental codes primarily intended for method development. A less publicized but no less important part of TURBOMOLE's mission has been educational: TURBOMOLE has provided a platform for training generations of students and postdocs, enabling them to participate in a large scientific software development enterprise. TURBOMOLE's user base soon extended beyond the computational chemistry community and now spans a diverse group of users across scientific disciplines in academia, education, government, and industry.

TURBOMOLE started as a semi-direct Hartree–Fock (HF) program with extensions for second-order Møller-Plesset perturbation theory[1–6] and time-dependent HF (TDHF) response properties.[7] TURBOMOLE was one of the first Gaussian basis function codes offering efficient semi-local density functional theory (DFT)[8] and time-dependent DFT (TDDFT) capabilities.[9] RI methods for DFT[10] and MP2 energies and gradients.[11,12]

In the 2000s, TURBOMOLE's DFT and TDDFT capabilities were overhauled and extended significantly by implementations enabling the computation of entire UV absorption and circular dichroism (CD) spectra,[13,14] infrared (IR)[15,16] and Raman[17] spectra, as well as improved ground-state DFT methods enabling DFT calculations for systems with close to 1000 atoms on single workstations.[18–20] In 2002 (TURBOMOLE V5.5), the `ricc2` program was added,[21] which enabled calculation of excitation energies using the approximate coupled-cluster singles and doubles method (CC2). Since then the `ricc2` program has been continuously extended to compute many linear and nonlinear properties and spectroscopic signatures. The `egrad` module was also first released in 2002, and has since become the cornerstone of TURBOMOLE's excited state gradient[22,23] and later nonadiabatic dynamics[24,25] and nonlinear optical property[26] capabilities within TDDFT and TDHF.

TURBOMOLE GmbH, a limited liability company located in Karlsruhe, Germany, was founded in 2007 as a vehicle to retain copyright of the code and to ensure continuity of TURBOMOLE development, maintenance, and distribution independent of individual developers. Starting with V5.10, TURBOMOLE was extended to explicitly account for spin–orbit (SO) coupling based on a two-component (2c) approach.[27,28] Here, the relativistic effects are introduced either by effective core potentials (ECPs) or by relativistic all-electron approaches based on decoupling the Dirac equation.[29,30] With V6.2, the software suite contained for the first time an explicitly correlated coupled-cluster code – now included in the `ccsdf12` module – for very accurate CCSD(F12)(T) calculations.[31] Available since V6.4, the `rirpa` module provided first efficient molecular implementation of the random-phase approximation (RPA) to ground state correlation energies.[32] In the past decade, `rirpa` was extended to include analytical gradients,[33] orbital self-consistent RPA,[34] and beyond-RPA methods,[35,36] providing a hierarchy of approximations to systematically validate and improve upon semilocal functionals.[36–38] The *GW* method was also implemented within the `escf` module to accurately calculate ionization energies and related properties in a post Kohn–Sham (KS) framework.[39–41]

Another milestone in TURBOMOLE's development was the extension to one-, two-, and three-dimensional periodic systems through the `riper` module,[42] initially at the semilocal DFT level, starting with V7.0, and recently extended to hybrid and range-separated functionals.[43] While the first implementation of local hybrid functionals (local hybrids) in TURBOMOLE employing a seminumerical exchange approximation dates back to 2012,[44] local hybrids[45] became available for a range of ground- and excited-state properties from V7.2 on.[46–49]

II. BASIS SETS

A. Orbital Basis Sets

From TURBOMOLE's beginnings, code development was accompanied by basis set development. Important first steps were the segmented-contracted basis sets for the elements up to Kr of double,[50] triple,[51] and later also quadruple-ζ valence quality,[52] which were energy-optimized at the Hartree–Fock level and extended by functions of higher angular quantum number for correlation and polarization. Karlsruhe double and triple-ζ basis sets were also generated for heavy elements[53] for the usage with ECPs. These basis sets have been the default choice in TURBOMOLE's input generator `define` since the mid-1990s, as indicated by the prefix "def-" and served as a very reasonable starting point for the development of a second generation of basis sets, the so-called "def2" bases.[54] These def2 bases were designed to yield similar errors for ground-state properties all across the *s*, *p*, and *d* elements of the periodic table and later[55] extended to *f* elements. For this, we created a benchmark set consisting of more than 300 molecules representing nearly each element in nearly all of its common oxidation states and changed or extended the preceding def bases where necessary. The def2 bases are available in double, triple, and quadruple-ζ valence quality with a smaller set of polarization functions for DFT treatments and a larger set for (post-)Hartree–Fock calculations. Typical errors for atomization energies (per atom) amount to 20/5/1 kJ/mol for the lower-polarized sets def2-SV(P)/TZVP/QZVP at DFT level and to 50/20/5 kJ/mol for the higher polarized sets def2-SVP/TZVPP/QZVPP at second-order Møller-Plesset theory and other correlated levels. For elements beyond Kr, the def2 system employs Wood–Boring (WB) ECPs for the *s*,[56,57] *d*,[58] and *f* elements[59] and Dirac–Hartree–Fock (DHF) ECPs *p* elements.[60,61]

Two-component self-consistent field methods, which became available in TURBOMOLE in 2007, required basis sets

TABLE I. Overview of the Karlsruhe or TURBOMOLE basis set families. The accuracy is stated by the mean absolute errors in the atomization energy (per atom) in kJ/mol at the DFT level for the test set described in Sec. II A with respect to a very large reference basis set representing the DFT basis set limit.[62,63] The standard deviation is given in parenthesis. Note that the errors of the def basis sets are measured with respect to def2-QZVPP.[54] The intended use and key features – taking the extensions into account – may serve as a guide for applications. Three types of auxiliary basis sets are considered: RI-*J* and RI-*K* at DFT/HF level, and auxiliary bases for post-HF/post-KS methods (see Sec. II C). Extensions for polarization effects (P) and spin–orbit coupling (-2c) are described in Sec. II A, whereas further extensions (D, -s) are described in Sec. II B.

Family	Accuracy			Key Features And Intended Use	Elements	Auxiliary Basis Sets	Extensions
	SV(P)	TZVP	QZVP				
def	7.7 (13.4)	10.9 (10.7)	–	Obsolete	H–Rn (no 4*f*)	RI-*J*, RI-*K* post-HF/post-KS	P
def2	11.8 (9.7)	3.8 (2.6)	1.0 (1.0)	General one-component calculations Electric properties, dispersion/noncovalent Application to post-HF and post-KS	H–Rn	RI-*J*, RI-*K* post-HF/post-KS	P, D
dhf	11.0 (9.5)	2.9 (1.9)	0.4 (0.4)	Similar to def2 but consistent DHF ECPs Correction of small deficits of def2 Two-component for heavier elements	H–Rn (no 4*f*)	RI-*J*, RI-*K*	P, -2c
x2c	6.2 (4.7)	1.9 (1.3)	–	Relativistic all-electron, finite nucleus model Core-region accessible, two-component for all	H–Rn	RI-*J*	P, -2c, -s

that describe the radial splitting of inner shells not included in the effective core potential. Starting from the def2 system, bases were optimized for the use together with one- and two-component DHF effective core potentials for Rb–Rn,[60,61,64–68] "dhf".[62] Already for one-component calculations they provide several improvements over the def2 system. Employing DHF ECPs throughout, they treat heavy elements up from the 5*s* row on the same footing. Additionally, several smaller deficits of the def2 system are corrected, for instance they feature a lower contraction length for the steepest *p* set in order to reduce the error in the atomization energies of *d*-element compounds and result in a better balance in errors for the different types of elements. For two-component calculations the dhf system provides extensions for the "valence-1" shells (for instance the 4*p*4*d* shells of the 5*p* elements), indicated by the suffix "-2c" in the basis set name. In two-component calculations the usage of these extensions is advisable, for instance in case of Bi_2, using the basis set extension changes the bond energy by about 15 kJ/mol at DFT level. Of course, their use is mandatory for all two-component calculations where the energies of the "valence-1" shells are of interest. Thus, the dhf system is well suited for clusters consisting of transition metals and main-group elements.[69–74]

Further developments became necessary with upcoming relativistic all-electron methods. Starting from the dhf system, we added functions for the inner shells and (energy-) optimized them at the exact two-component (X2C) level employing a finite-size nucleus model.[63] Presently, they are available in their one- and two-component variants (without and with suffix "-2c") at double and triple-ζ quality together with optimized resolution-of-the-identity (RI-*J*) auxiliary bases,[63] quadruple-ζ bases will be available soon. Additionally to the accuracy assessment for ground state properties, special care was taken for the atomic orbital energies, in particular for the inner shells. For instance, for the x2c-TZVP-2c basis basis set induced errors are below 1 eV even for the innermost shells of the 6*p* elements (for both HF and DFT), which is very little compared to the orbital energies themselves amounting to several ten thousand eV, and also compared to method-induced changes of several ten to several hundred eV.

B. Basis Sets Extensions for Specific Properties

Calculations of properties sometimes require basis functions that have only very small contributions to ground-state energies and thus cannot be determined by energy optimization.[54,55,62,63,75] Their need – in particular in case of diffuse functions – has to be balanced carefully against performance considerations, as such functions lower the efficiency of integral screening and may lead to linear dependence problems. Basis sets extensions for excited state calculations and related properties such as polarizabilities[76] address this issue by choosing the basis set parameters to maximize atomic Hartree–Fock polarizabilities based on the variational principle.

The successful optimization strategy started from the def2 basis sets of split-valence to quadruple-ζ valence quality[54] and augments them sparingly using diffuse basis functions. The resulting property-optimized basis sets differ from the larger augmented correlation-consistent basis sets (aug-cc-pV*X*Z, *X* = D, T, Q) [77–79] in two significant respects. They only add diffuse basis functions with angular momenta of at most one larger than that of the highest occupied atomic orbital. Moreover, the number of added diffuse basis functions does not increase with the size of the underlying orbital basis set. This allows for augmented basis sets that are smaller and less diffuse but provide similar accuracy as the aug-cc-pV*X*Z augmented basis sets, which were obtained by optimizing energies of atomic anions or by extrapolation.[76]

While the property-optimized basis set extensions were optimized for HF polarizabilities, they are also applicable to other molecular properties and electronic structure methods.

def2-SVPD have been successfully utilized to study electronic excitations and dielectric constants in oligomers of benzimidazobenzophenanthroline (BBL), which are of interest for organic photovoltaics (Figure 1).[80] Being relatively compact, the def2-SVPD basis sets are a good choice for calculating properties of large molecules with time-dependent DFT (TDDFT). At the same time, property-optimized basis sets yield good accuracy for computing non-bonding interaction energies in the S22 benchmark[81] of small and medium-sized molecules consisting of first- and second-row elements with density functional theory.[82] In combination with optimized auxiliary basis sets, they perform as well as aug-cc-pVXZ basis sets in the S22 benchmark with the second-order Møller–Plesset theory using the resolution-of-identity approximation (RI-MP2).[83] An application to hyperpolarizabilities is presented in the main text

Tailored basis sets are not only required for electrical properties but also for magnetic properties. The nuclear magnetic resonance shielding tensor depends on the density in the vicinity of the nuclei.[86,87] This is especially problematic in relativistic calculations where the density is subject to a spatial contraction. Here, tight functions are added and the contraction of the innermost segment of the x2c-type basis sets is re-optimized. A minimal number of additional functions is then added by minimizing the differences of nuclear magnetic resonance (NMR) shielding constants with respect to a very large reference basis set for all closed-shell molecules of the above-mentioned test set. The basis set feature the suffix "-s".[88] The additional functions result in a significant improvement by halving the deviation from a large even-tempered reference basis yet conserving the compactness of the underlying x2c-TZVPall basis set.[63,88] The error is smaller than for the uncontracted Dyall-VTZ basis set,[89–94] which has nearly double the number of functions. Similar results are obtained for the corresponding double-ζ basis set, x2c-SVPall-s.

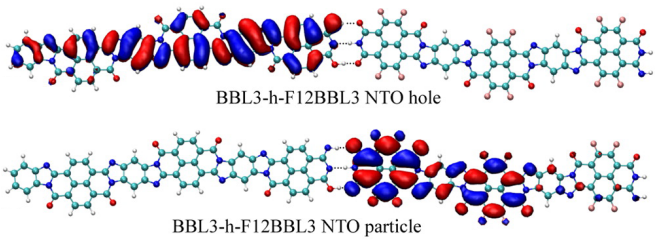


FIG. 1. Natural transition orbitals (NTOs)[84] of benzimidazobenzophenanthroline trimer (BBL3) / fluorinated BBL trimer (F12BBL3) hydrogen-bonded complex computed with TDDFT using PBE0 exchange–correlation functional[85] and def2-SVPD basis sets. Reprinted with permission from S. Kraner, R. Scholz, C. Koerner, and K. Leo, Design Proposals for Organic Materials Exhibiting a Low Exciton Binding Energy. *J. Phys. Chem. C* **2015**, *119*, 22820-22825. Copyright 2015 American Chemical Society.

C. Auxiliary Basis Sets

RI methods, which were available in TURBOMOLE very early, required the development of accurate auxiliary basis sets. The key design goal was to keep the error of the RI approximation at least one order of magnitude smaller than the incompleteness error of the corresponding orbital basis sets. For the Coulomb integrals a first attempt was made together with the def orbital bases.[53] Developments continued with improved RI-J[95] and RI-K[96] auxiliary basis sets that are in line with the design goal also for the comparably small orbital basis set errors of the quadruple-ζ valence bases. It turned out that for Coulomb and also exchange integrals one auxiliary basis (per element) is sufficient for all types of orbital bases, as the corresponding operators depend only on products of occupied orbitals, which do not change that much when changing the orbital basis. Matters are different for correlated treatments, where products of occupied and virtual orbitals need to be fitted. Here, a specific auxiliary basis needs to be designed and optimized for each (type of) orbital basis to reach the design goal. Furthermore, in contrast to Coulomb and exchange energies, no variation principle holds for RI-approximated correlation energies. The first step towards reliable auxiliary bases for correlated treatments thus was the formulation of a suited error functional, which was presented together with RI-MP2 auxiliary bases for the def-SVP and def-TZVPP orbital bases.[12] An analytic implementation of basis set gradients for this functional presented in Ref. 97 facilitated the optimization of the auxiliary basis sets also for large very accurate orbitals basis sets. Later this was applied for the def2 bases[83,97–99] and the correlation-consistent basis sets.[97,100,101]

III. EPR SPECTRA

Electron paramagnetic resonance (EPR) parameters for open-shell systems are influenced crucially by spin–orbit effects and are best treated by four- or two-component computations. The two-component implementation in TURBOMOLE[27,29,30,44,102] has recently been used at both X2C and DKH levels to extract generalized exchange tensors for trinuclear spin-coupled 3d complexes.[103] In this approach, which presently is available only in a local version of TURBOMOLE, the computed energies of different collinear and non-collinear generalized broken-symmetry states are mapped onto an effective spin Hamiltonian. This yields isotropic and anisotropic contributions to the exchange tensors with reasonable accuracy.[103] The well-known overestimation of spin–orbit interactions when neglecting two-electron contributions is corrected by employing the atomic mean-field spin–orbit approximation (AMFSO)[104] or the (modified) screened nuclear spin-orbit (SNSO) approach,[30,105,106] for the latter in a simple and computationally cheap manner. Both approximations provide hyperfine couplings and g-tensors in excellent agreement with recent four-component Dirac–Kohn–Sham results for 3d, 4d, and 5d transition-metal complexes, when combined with the X2C or DKH picture-change corrected integrals,[107] in a clear improvement over perturbational

treatments of spin–orbit coupling. The AMFSO approximation furthermore allows to evaluate the so-called spin–other-orbit term arising due to the relativistic Gaunt term, which also was found to be of largest relative importance for the 3*d* systems.[107] We note in passing that TURBOMOLE also features a spin–orbit mean field (SOMF) implementation without a one-center approximation to treat spin–orbit coupling perturbationally based at the one-component approach.[108] The two-component implementation has meanwhile been extended to local hybrid functionals, and the importance of the choice of the functional for the hyperfine couplings of heavier transition metals has been investigated.[109]

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