

Calibration of Cholesky Auxiliary Basis Sets for Multiconfigurational Perturbation Theory Calculations of Excitation Energies

Jonas Boström,[†] Mickaël G. Delcey,[†] Francesco Aquilante,[‡] Luis Serrano-Andrés,[¶]
Thomas Bondo Pedersen,[§] and Roland Lindh^{*,†}

*Department of Theoretical Chemistry, Chemical Center, University of Lund,
P. O. Box 124 S-221 00 Lund, Sweden, Department of Physical Chemistry, Sciences II,
University of Geneva, Quai E. Ansermet 30, 1211 Geneva 4, Switzerland, Instituto de
Ciencia Molecular, Universitat de València, P. O. Box 22085, ES-46071 Valencia, Spain,
and Centre for Theoretical and Computational Chemistry, Department of Chemistry,
University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway*

Received November 19, 2009

Abstract: The accuracy of auxiliary basis sets derived from Cholesky decomposition of two-electron integrals is assessed for excitation energies calculated at the state-average complete active space self-consistent field (CASSCF) and multiconfigurational second order perturbation theory (CASPT2) levels of theory using segmented as well as generally contracted atomic orbital basis sets. Based on 196 valence excitations in 26 organic molecules and 72 Rydberg excitations in 3 organic molecules, the results show that Cholesky auxiliary basis sets can be used without compromising the accuracy of the multiconfigurational methods. Specifically, with a decomposition threshold of 10^{-4} au, the mean error due to the Cholesky auxiliary basis set is 0.001 eV, or smaller, decreasing with increasing atomic orbital basis set quality.

1. Introduction

Given a Gaussian atomic orbital (AO) basis χ and an auxiliary basis φ , density fitting (DF) consists of determining a set of fitting coefficients C such that $\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \approx \sum_K C_{\mu\nu}^K \varphi_K(\mathbf{r})$. In the most common DF approach, this amounts to the minimization of the following positive semidefinite error matrix

$$\Delta_{\mu\nu} = \left(\chi_\mu \chi_\nu - \sum_K C_{\mu\nu}^K \varphi_K \right) \chi_\mu \chi_\nu - \sum_K C_{\mu\nu}^K \varphi_K \quad (1)$$

where $(\cdot|\cdot)$ is a two-electron integral in Mulliken notation. Clearly, the error matrix can be made arbitrarily small, i.e., essentially exact, by a suitable choice of auxiliary basis set.

As an alternative to standard auxiliary basis sets, which are preoptimized to reproduce specific energy contributions (Coulomb, exchange, second-order dynamic correlation), we have recently proposed to determine the auxiliary basis functions on-the-fly by means of Cholesky decomposition (CD) of the entire or parts of the two-electron integral matrix in the AO basis.^{1–4} An upshot of this approach is that the decomposition threshold directly specifies an upper bound to the error matrix $\Delta_{\mu\nu}$ in eq 1. In the full-CD approach,^{5,6} the entire molecular two-electron integral matrix is Cholesky decomposed until all elements of the error matrix are below the specified decomposition threshold. One-center CD (1C-CD)¹ differs from full-CD in that only those elements of the error matrix for which χ_μ and χ_ν are centered on the same atom are bounded by the decomposition threshold. The atomic CD (aCD)¹ auxiliary basis sets are constructed by a decomposition of the atomic integral matrix, and like 1C-CD, only one-center errors are bounded by the decomposition threshold. Finally, the recently proposed atomic compact CD (acCD)⁴ auxiliary basis sets are constructed from the aCD

* To whom correspondence should be addressed- E-mail: roland.lindh@teokem.lu.se.

[†] Lund University.

[‡] University of Geneva.

[¶] Universitat de València.

[§] University of Oslo.

ones by reducing the number of primitive Gaussians in the product functions. By removing the auxiliary functions with the highest angular momenta, the aCD and acCD sets can be brought to a size (number of auxiliary basis functions) similar to the standard sets, thus mitigating the issues raised concerning the efficiency of CD auxiliary basis sets.⁷ The CD auxiliary basis sets offer several advantages such as complete freedom in selection of the atomic orbital (AO) basis set, an unbiased nature with respect to the wave function or density functional model, and nearly arbitrary control over the associated error. For a detailed discussion of the CD approach, we refer to the recent review by Pedersen et al.³

We have previously demonstrated the accuracy of the full-CD, 1C-CD, aCD, and acCD auxiliary basis sets for calculations of electronic ground state energies at the Hartree–Fock (HF), second-order Møller–Plesset (MP2), and hybrid as well as nonhybrid density functional theory (DFT) levels of theory with a range of AO basis sets.⁸ Here, we proceed with the accuracy assessment of the CD auxiliary basis sets in conjunction with the complete active space self-consistent field (CASSCF)^{9–11} and multiconfigurational second order perturbation theory (CASPT2)^{12–14} approaches to the computation of vertical electronic excitation energies. Whereas the earlier investigation⁸ monitored the accuracy of the CD auxiliary basis set in association with the ground states of the closed-shell molecules in the G2/97 test suite, the present investigation aims at measuring the accuracy of excited electronic states. For this purpose, the Schreiber test suite^{15,16} has been employed. Recalling that even in the recent past AO basis sets beyond 300–400 functions were prohibitive, a number of recent applications employing 1000–1500 Gaussian basis functions^{11,14,17–19} have clearly demonstrated the computational advantage of the CD-based CASSCF/CASPT2 approach. A major goal of the present study therefore is to establish accuracy standards, i.e., decomposition thresholds, for future reference.

Hättig and co-workers^{20–23} have used auxiliary basis sets optimized for dynamic correlation (at the MP2 level) for the calculation of excitation energies and excited state properties with the second-order coupled cluster (CC2) model,²⁴ and Pedersen et al.^{25–29} have used full-CD to calculate electric dipole polarizability and optical rotation from the CC2 linear response function which, formally, includes a summation over all (singlet) excited electronic states. A major difference between these two approaches is that in the CD case the same auxiliary basis set is used in all stages of the calculation including the computation of the HF reference function. That is, the same CD auxiliary basis set is used for Coulomb, exchange, and dynamic correlation contributions. At the DFT level, studies of the performance of preoptimized auxiliary basis sets for excitation energy calculations limited to the nonhybrid BP86 functional^{30,31} have been reported by Bauernschmitt et al. and Rappoport and Furche.^{32,33} Neese and co-workers^{34,35} have extended these calibrations to a hybrid DFT functional. However, as we can judge from the technical details of the latter two studies, the RI approximation was not used in the ground state hybrid DFT calculations. Nevertheless, in these studies, the performance

of auxiliary basis sets in accurately approximating the J and K type MO integrals used in the time dependent DFT (TDDFT) equations has been documented. To our knowledge, no benchmark studies have been presented in which a single auxiliary basis set has been calibrated with respect to both the ground state DFT energies and TD-DFT excitation energies using hybrid functionals. Considering the fact that the same CD auxiliary basis set is used for Coulomb, exchange, and static and dynamic correlation as modeled by the CASSCF/CASPT2 approach, there are strong reasons to believe that the results presented here can be directly transferred to nonhybrid DFT functionals and other wave function models used for excited state calculations.

2. Computational Details

The purpose of the present benchmark study is not to assess the accuracy of the CASPT2/CASSCF method in comparison with other quantum chemical models or experiments. Rather, we wish to test that the CD auxiliary basis sets can in an unbiased way be used to describe excited states, i.e., the ability of the CD auxiliary basis sets to accurately represent two-electron integrals involving virtual molecular orbitals. We use the CASSCF/CASPT2 protocol as a successful representative of the methods for computing excitation energies. Two test suites are employed. The first was designed by Schreiber et al.¹⁵ and includes 196 vertical excitation energies, both singlet and triplet excited states, for 26 organic molecules. The excitations are mainly of a $\pi-\pi^*$ or $n-\pi^*$ nature with some $\sigma-\pi^*$ excitations. The second set was designed to test for Rydberg states. These calculations involve valence and Rydberg singlet and triplet states for ethene, *trans*-1,3-butadiene, and formamide. Here, we report statistics based on the 72 transitions involving the Rydberg states.

For the first series, the details of the computations are as follows: For molecules of high symmetry, the conventional as well as DF-based CASPT2 method, as currently implemented, fails to correctly preserve the degeneracy of states belonging to multidimensional irreducible representations. This would lead to reference data for degenerate states with a small artificial symmetry breaking. Even when this has no practical consequences for the interpretation of the excited states, complications in the analysis of the CD auxiliary basis set error are avoided by excluding the triazine and benzene molecules from the original test suite in this work. Geometries, active spaces, and other information needed to perform the calculations were chosen exactly as in the work of Schreiber et al.,¹⁵ although we have extended the study to include four different AO basis sets. In addition to the original TZVP³⁶ basis set, the ANO-RCC-VXZP^{37,38} ($X = D, T, Q$) AO basis sets were used. We note that, whereas the TZVP basis set was designed for the HF method, the ANO-RCC-VXZP sets were specifically designed in combination with the CASSCF/CASPT2 paradigm. However, the aim of this study is not to investigate the quality of the AO basis set with respect to the accuracy of excitation energies in comparison with experimental or “exact” excitation energies. Rather, we will only comment on the ability of

the CD auxiliary basis set to approximate integrals with the four different AO basis sets used in this study.

For the second series of benchmark calculations (the Rydberg benchmark), basis sets of the ANO-L type³⁷ contracted to C, N, O [4s3p1d]/H [2s1p] were employed (almost a full VTZP basis), supplemented by a set of 1s1p1d diffuse functions centered in the molecular cation charge centroid and whose exponents and coefficients were determined elsewhere.^{39–41} The employed active spaces included the full valence π space (and the oxygen lone pair in formamide) plus the nine 3s3p3d Rydberg orbitals, leading to spaces (electrons, orbitals) (2,11), (4,13), and (6,13) for ethene, *trans*-1,3-butadiene, and formamide, respectively. The low-lying valence and Rydberg singlet and triplet states were computed, including the Rydberg series π (HOMO) \rightarrow 3s3p3d and also $n \rightarrow$ 3s3p3d for formamide. The multistate (MS) CASPT2 method⁴² was employed in order to take into account the valence-Rydberg mixing effect displayed at the CASSCF level of theory. The imaginary level-shift technique⁴³ was used with a parameter of 0.1 au to prevent the presence of weakly coupling intruder states. Geometries and basis sets were those used previously for ethene,³⁹ *trans*-1,3-butadiene,³⁹ and formamide.⁴⁰

Calculations have been performed in these two series with the full-CD, aCD, and acCD auxiliary basis sets obtained with decomposition thresholds of 10^{-3} , 10^{-4} , 10^{-5} , and 10^{-6} au. The auxiliary basis set pruning technique (skipping higher angular components, SHAC), as used in our previous benchmark study,⁸ was explored too. While the 1C-CD has been excluded from the present work for implementation reasons—the method has not been implemented for cases with point group symmetry—the aCD and acCD results should be representative of 1C-CD, as they were in our previous report on ground state energies.⁸ The computed total and excitation energies were compared to reference energies compiled with conventional CASSCF/CASPT2.^{13,44} For uracil, cytosine, thymine, adenine, and octatetraene with ANO-RCC-VQZP in the first test series, the numbers of AO basis functions are 560, 590, 675, 700, and 740, respectively. This number of functions is prohibitive for conventional CASSCF/CASPT2 calculations. In these cases, full-CD calculations with a Cholesky threshold of 10^{-10} au were used as a reference.

All calculations were performed with the MOLCAS 7 program package⁴⁵ using the CD-based implementations described by Aquilante et al.^{11,14}

3. Results and Discussion

The accuracy of the CD auxiliary basis sets that we aim to establish should be compared to the accuracy of standard preoptimized auxiliary basis sets. It has been shown with TD-DFT calculations on 36 excited states for a set of small molecules (the largest being benzene) that errors in adiabatic excitation energies are not higher than 0.03 eV.³³ These results are in line with the earlier reported accuracy assessment by Bauernschmitt and co-workers on 19 vertical excitation energies.³² We note that the results of Bauernschmitt et al.³² and Rappoport and Furche³³ are based on the original TZVP auxiliary basis set of Eichkorn et al.,⁴⁶

which was designed for ground state calculations with nonhybrid DFT functionals. This auxiliary basis set was subsequently augmented by “downward extrapolation” including primitive Gaussians to improve the quality of the results. We stress two major differences between these benchmark studies and those of the current report. First, the present CD auxiliary basis sets are designed on-the-fly in a procedure with error control (in the sense of eq 1) via a single parameter, the decomposition threshold. Second, whereas the previous studies are based on nonhybrid DFT calculations, the current test includes Coulomb and exchange as well as correlation.

In the rest of this section, the accuracy of the CASSCF/CASPT2 excitation energies as a function of the CD approach and threshold, auxiliary basis set pruning, and AO basis set saturation is analyzed. We report mean errors, mean absolute errors, maximum errors, and standard deviations for excitation energies at the CASPT2 and CASSCF levels of approximation in Tables 1–8. The CASPT2 results are representative for the CASSCF results; hence, the CASSCF results, Tables 5–8, are included in the Supporting Information. Our findings and observations can be summarized as follows.

Cancellation of Errors. In one of the earliest investigations into the accuracy of CD auxiliary basis sets,¹ absolute and activation energies of 20 reactions were analyzed. In that study, we observed a favorable cancellation of errors with respect to the activation energies. Typically, the auxiliary basis set error was reduced by a factor of 2–4 in these cases. For the computation of vertical excitation energies, we would expect error cancellation to be at its optimum. In Figure 1, results obtained with the TZVP basis set and the full-CD, aCD, and acCD auxiliary basis sets are displayed.

A reduction of the mean absolute error for the same CD threshold of as much as 1 order of magnitude is observed going from total energies to excitation energies (compare the center and right panels of Figure 1). For total energies we see significant differences with respect to the full-CD, aCD, and acCD approximations as compared with the excitation energies. Here, we also note that the difference between the aCD and acCD auxiliary basis sets with and without auxiliary basis set pruning (SHAC) is significant. However, for the excitation energies, the discrepancy between the aCD and acCD auxiliary basis sets, with or without SHAC, is nearly completely removed. These trends hold true for any of the other AO basis sets in this study. Furthermore, we note that the mean absolute errors of the excitation energies are well below 0.01 eV already for the highest CD threshold of 10^{-3} au. We also note that, while full-CD shows an exponential decay of the mean absolute excitation energy error as a function of the CD threshold, the aCD and acCD auxiliary basis sets exhibit an error which is virtually constant and on the order of 0.001 eV. This suggests that the CD threshold can be increased by 1 order of magnitude when calculating excitation energies compared to total energy calculations.⁸ We also note that auxiliary basis set pruning can be used in the computation of excitation energies, thus speeding up the calculations by reducing the number of auxiliary functions.

Table 1. Mean Errors in eV for CASPT2 Excitation Energies as a Function of AO Basis Set, CD Threshold (in au), and CD Auxiliary Basis Set (without and with pruning)

basis set	CD-thres.	mean errors for CASPT2 calculations				
		full-CD	aCD	acCD	(SHAC)	
					aCD	acCD
TZVP	10 ⁻³ au	-3.7 × 10 ⁻³	-1.0 × 10 ⁻³	-1.2 × 10 ⁻³	3.4 × 10 ⁻³	3.2 × 10 ⁻³
	10 ⁻⁴ au	-7.6 × 10 ⁻⁴	-5.9 × 10 ⁻⁴	-5.9 × 10 ⁻⁴	3.8 × 10 ⁻⁴	4.3 × 10 ⁻⁴
	10 ⁻⁵ au	-1.1 × 10 ⁻⁴	-1.5 × 10 ⁻⁴	-1.5 × 10 ⁻⁴	5.4 × 10 ⁻⁴	5.4 × 10 ⁻⁴
	10 ⁻⁶ au	6.6 × 10 ⁻⁶	-1.7 × 10 ⁻⁴	-1.7 × 10 ⁻⁴	5.5 × 10 ⁻⁴	5.5 × 10 ⁻⁴
ANO-RCC-VDZP	10 ⁻³ au	-2.6 × 10 ⁻³	4.6 × 10 ⁻⁵	2.5 × 10 ⁻⁵	1.3 × 10 ⁻³	1.3 × 10 ⁻³
	10 ⁻⁴ au	7.9 × 10 ⁻⁶	5.2 × 10 ⁻⁵	2.6 × 10 ⁻⁵	1.2 × 10 ⁻³	1.2 × 10 ⁻³
	10 ⁻⁵ au	-8.6 × 10 ⁻⁶	5.4 × 10 ⁻⁵	6.0 × 10 ⁻⁵	9.7 × 10 ⁻⁴	9.9 × 10 ⁻⁴
	10 ⁻⁶ au	-2.3 × 10 ⁻⁶	5.7 × 10 ⁻⁵	5.4 × 10 ⁻⁵	9.2 × 10 ⁻⁴	9.3 × 10 ⁻⁴
ANO-RCC-VTZP	10 ⁻³ au	3.9 × 10 ⁻³	4.2 × 10 ⁻⁵	1.2 × 10 ⁻⁵	1.6 × 10 ⁻⁴	1.4 × 10 ⁻⁴
	10 ⁻⁴ au	1.2 × 10 ⁻⁴	3.1 × 10 ⁻⁵	-1.2 × 10 ⁻⁵	1.4 × 10 ⁻⁴	1.2 × 10 ⁻⁴
	10 ⁻⁵ au	5.3 × 10 ⁻⁶	8.3 × 10 ⁻⁶	2.4 × 10 ⁻⁶	1.2 × 10 ⁻⁴	1.2 × 10 ⁻⁴
	10 ⁻⁶ au	-5.3 × 10 ⁻⁶	2.3 × 10 ⁻⁶	1.5 × 10 ⁻⁶	1.1 × 10 ⁻⁴	1.1 × 10 ⁻⁴
ANO-RCC-VQZP	10 ⁻³ au	-1.7 × 10 ⁻³	9.4 × 10 ⁻⁶	-1.4 × 10 ⁻⁶	5.1 × 10 ⁻⁵	-2.5 × 10 ⁻⁵
	10 ⁻⁴ au	-5.2 × 10 ⁻⁴	2.2 × 10 ⁻⁷	-1.9 × 10 ⁻⁶	1.8 × 10 ⁻⁵	-2.8 × 10 ⁻⁵
	10 ⁻⁵ au	-3.1 × 10 ⁻⁵	9.7 × 10 ⁻⁸	1.2 × 10 ⁻⁶	1.7 × 10 ⁻⁵	1.6 × 10 ⁻⁵
	10 ⁻⁶ au	2.6 × 10 ⁻⁶	2.3 × 10 ⁻⁷	1.0 × 10 ⁻⁷	1.5 × 10 ⁻⁵	1.4 × 10 ⁻⁵
ANO-L + Rydberg ^a	10 ⁻³ au	-6.6 × 10 ⁻⁴	1.5 × 10 ⁻⁵	7.2 × 10 ⁻⁶	-1.6 × 10 ⁻⁴	-4.6 × 10 ⁻⁵
	10 ⁻⁴ au	-4.2 × 10 ⁻⁵	1.5 × 10 ⁻⁵	1.7 × 10 ⁻⁵	-1.8 × 10 ⁻⁴	-1.3 × 10 ⁻⁴
	10 ⁻⁵ au	9.2 × 10 ⁻⁶	1.4 × 10 ⁻⁵	1.5 × 10 ⁻⁵	-1.5 × 10 ⁻⁴	-2.0 × 10 ⁻⁴
	10 ⁻⁶ au	7.9 × 10 ⁻⁶	2.1 × 10 ⁻⁵	2.0 × 10 ⁻⁵	-1.2 × 10 ⁻⁴	-1.5 × 10 ⁻⁴

^a ANO-L C, N, O [4s3p1d]/H[2s1p] with explicit molecule-centered [1s1p1d] Rydberg functions.**Table 2.** Standard Deviations in eV for CASPT2 Excitation Energies as a Function of AO Basis Set, CD Threshold (in au), and CD Auxiliary Basis Set (without and with pruning)

basis set	CD-thres.	standard deviations for CASPT2 calculations				
		full-CD	aCD	acCD	(SHAC)	
					aCD	acCD
TZVP	10 ⁻³ au	4.7 × 10 ⁻³	1.1 × 10 ⁻³	1.1 × 10 ⁻³	7.0 × 10 ⁻³	6.7 × 10 ⁻³
	10 ⁻⁴ au	5.7 × 10 ⁻⁴	4.1 × 10 ⁻⁴	4.1 × 10 ⁻⁴	7.8 × 10 ⁻⁴	8.2 × 10 ⁻⁴
	10 ⁻⁵ au	1.2 × 10 ⁻⁴	2.3 × 10 ⁻⁴	2.2 × 10 ⁻⁴	6.4 × 10 ⁻⁴	6.4 × 10 ⁻⁴
	10 ⁻⁶ au	4.2 × 10 ⁻⁵	2.2 × 10 ⁻⁴	2.2 × 10 ⁻⁴	6.4 × 10 ⁻⁴	6.4 × 10 ⁻⁴
ANO-RCC-VDZP	10 ⁻³ au	6.5 × 10 ⁻³	5.9 × 10 ⁻⁴	4.3 × 10 ⁻⁴	1.3 × 10 ⁻³	1.2 × 10 ⁻³
	10 ⁻⁴ au	6.5 × 10 ⁻⁴	6.3 × 10 ⁻⁴	6.7 × 10 ⁻⁴	1.3 × 10 ⁻³	1.4 × 10 ⁻³
	10 ⁻⁵ au	1.3 × 10 ⁻⁴	6.3 × 10 ⁻⁴	5.5 × 10 ⁻⁴	1.3 × 10 ⁻³	1.3 × 10 ⁻³
	10 ⁻⁶ au	1.1 × 10 ⁻⁵	6.5 × 10 ⁻⁴	6.4 × 10 ⁻⁴	1.3 × 10 ⁻³	1.2 × 10 ⁻³
ANO-RCC-VTZP	10 ⁻³ au	4.4 × 10 ⁻²	5.0 × 10 ⁻⁴	1.3 × 10 ⁻⁴	5.0 × 10 ⁻⁴	1.6 × 10 ⁻⁴
	10 ⁻⁴ au	1.5 × 10 ⁻³	3.6 × 10 ⁻⁴	9.5 × 10 ⁻⁵	3.6 × 10 ⁻⁴	1.5 × 10 ⁻⁴
	10 ⁻⁵ au	6.0 × 10 ⁻⁵	1.0 × 10 ⁻⁴	4.0 × 10 ⁻⁵	1.3 × 10 ⁻⁴	9.5 × 10 ⁻⁵
	10 ⁻⁶ au	8.4 × 10 ⁻⁵	2.2 × 10 ⁻⁵	1.3 × 10 ⁻⁵	8.0 × 10 ⁻⁵	8.0 × 10 ⁻⁵
ANO-RCC-VQZP	10 ⁻³ au	2.4 × 10 ⁻²	1.3 × 10 ⁻⁴	5.5 × 10 ⁻⁵	4.0 × 10 ⁻⁴	4.7 × 10 ⁻⁴
	10 ⁻⁴ au	4.2 × 10 ⁻³	5.1 × 10 ⁻⁶	1.1 × 10 ⁻⁵	2.5 × 10 ⁻⁵	5.5 × 10 ⁻⁴
	10 ⁻⁵ au	1.9 × 10 ⁻⁴	3.0 × 10 ⁻⁶	1.8 × 10 ⁻⁵	2.4 × 10 ⁻⁵	1.9 × 10 ⁻⁵
	10 ⁻⁶ au	3.6 × 10 ⁻⁵	3.7 × 10 ⁻⁶	2.3 × 10 ⁻⁶	1.9 × 10 ⁻⁵	2.3 × 10 ⁻⁵
ANO-L + Rydberg ^a	10 ⁻³ au	1.7 × 10 ⁻³	8.9 × 10 ⁻⁵	9.9 × 10 ⁻⁵	8.9 × 10 ⁻⁴	8.8 × 10 ⁻⁴
	10 ⁻⁴ au	1.9 × 10 ⁻⁴	9.0 × 10 ⁻⁵	9.1 × 10 ⁻⁵	8.3 × 10 ⁻⁴	9.2 × 10 ⁻⁴
	10 ⁻⁵ au	6.4 × 10 ⁻⁵	9.0 × 10 ⁻⁵	9.0 × 10 ⁻⁵	5.7 × 10 ⁻⁴	6.1 × 10 ⁻⁴
	10 ⁻⁶ au	2.9 × 10 ⁻⁵	8.7 × 10 ⁻⁵	8.7 × 10 ⁻⁵	5.7 × 10 ⁻⁴	5.9 × 10 ⁻⁴

^a ANO-L C, N, O [4s3p1d]/H[2s1p] with explicit molecule-centered [1s1p1d] Rydberg functions.**AO Basis Set Convergence and CD Approximations.**

It has previously been observed⁸ that the accuracy of the CD auxiliary basis sets for a given set of CD parameters (threshold and high angular momentum eliminations) improves with increased AO basis set quality. In Figure 2, this can be analyzed in the case of excitation energies for ANO-RCC-VXZP.

Here, we again note that, as the AO basis set is improved in the sequence X = D, T, Q, the overall accuracy is improved. While it is natural that this trend is less clear for the full-CD results, it is significant that it occurs for the aCD and acCD auxiliary basis sets. In particular, for the largest

AO basis set, a rather loose threshold for aCD can be used without affecting the accuracy of the computed excitation energy. Furthermore, in comparing the different CD approaches, it is noted that the aCD and acCD with a CD threshold of 10⁻³ au can be used as a standard for all practical purposes. At this level of approximation, the errors due to the use of CD auxiliary basis sets can be ignored.

Pruned aCD and acCD Auxiliary Basis Sets. By construction, the aCD and acCD auxiliary basis sets include high angular momentum components. In an *ad hoc* pruning of the auxiliary basis sets, based on the reasoning that the

Table 3. Maximum Errors in eV for CASPT2 Excitation Energies as a Function of AO Basis Set, CD Threshold (in au), and CD Auxiliary Basis Set (without and with pruning)

basis set	CD-thres.	maximum errors for CASPT2 calculations				
		full-CD	aCD	acCD	(SHAC)	
					aCD	acCD
TZVP	10 ⁻³ au	-2.0 × 10 ⁻²	-8.1 × 10 ⁻³	-7.5 × 10 ⁻³	3.0 × 10 ⁻²	2.9 × 10 ⁻²
	10 ⁻⁴ au	-2.2 × 10 ⁻³	-2.1 × 10 ⁻³	-2.1 × 10 ⁻³	2.6 × 10 ⁻³	3.0 × 10 ⁻³
	10 ⁻⁵ au	7.5 × 10 ⁻⁴	-1.4 × 10 ⁻³	-1.4 × 10 ⁻³	2.2 × 10 ⁻³	2.2 × 10 ⁻³
	10 ⁻⁶ au	3.2 × 10 ⁻⁴	-1.4 × 10 ⁻³	-1.4 × 10 ⁻³	2.2 × 10 ⁻³	2.2 × 10 ⁻³
ANO-RCC-VDZP	10 ⁻³ au	-3.3 × 10 ⁻²	-7.1 × 10 ⁻³	-5.5 × 10 ⁻³	-7.1 × 10 ⁻³	-5.5 × 10 ⁻³
	10 ⁻⁴ au	-6.0 × 10 ⁻³	-8.2 × 10 ⁻³	-7.9 × 10 ⁻³	-8.2 × 10 ⁻³	-8.4 × 10 ⁻³
	10 ⁻⁵ au	-1.1 × 10 ⁻³	-8.2 × 10 ⁻³	-6.9 × 10 ⁻³	-9.4 × 10 ⁻³	-9.4 × 10 ⁻³
	10 ⁻⁶ au	-9.0 × 10 ⁻⁵	-8.7 × 10 ⁻³	-8.5 × 10 ⁻³	-8.7 × 10 ⁻³	-8.5 × 10 ⁻³
ANO-RCC-VTZP	10 ⁻³ au	5.9 × 10 ⁻¹	6.9 × 10 ⁻³	1.6 × 10 ⁻³	6.9 × 10 ⁻³	1.7 × 10 ⁻³
	10 ⁻⁴ au	1.6 × 10 ⁻²	5.0 × 10 ⁻³	-1.2 × 10 ⁻³	5.0 × 10 ⁻³	-1.2 × 10 ⁻³
	10 ⁻⁵ au	5.6 × 10 ⁻⁴	1.4 × 10 ⁻³	5.4 × 10 ⁻⁴	1.4 × 10 ⁻³	5.4 × 10 ⁻⁴
	10 ⁻⁶ au	-1.1 × 10 ⁻³	3.0 × 10 ⁻⁴	1.3 × 10 ⁻⁴	3.3 × 10 ⁻⁴	3.6 × 10 ⁻⁴
ANO-RCC-VQZP	10 ⁻³ au	-3.1 × 10 ⁻¹	1.8 × 10 ⁻³	-6.7 × 10 ⁻⁴	5.5 × 10 ⁻³	-6.4 × 10 ⁻³
	10 ⁻⁴ au	-5.5 × 10 ⁻²	7.0 × 10 ⁻⁵	-1.2 × 10 ⁻⁴	2.2 × 10 ⁻⁴	-7.7 × 10 ⁻³
	10 ⁻⁵ au	-1.9 × 10 ⁻³	4.0 × 10 ⁻⁵	2.5 × 10 ⁻⁴	2.1 × 10 ⁻⁴	-6.1 × 10 ⁻⁵
	10 ⁻⁶ au	5.0 × 10 ⁻⁴	4.8 × 10 ⁻⁵	3.0 × 10 ⁻⁵	-6.1 × 10 ⁻⁵	-1.7 × 10 ⁻⁴
ANO-L + Rydberg ^a	10 ⁻³ au	4.7 × 10 ⁻³	-4.7 × 10 ⁻⁴	-4.6 × 10 ⁻⁴	-2.9 × 10 ⁻³	-2.9 × 10 ⁻³
	10 ⁻⁴ au	5.9 × 10 ⁻⁴	-4.7 × 10 ⁻⁴	-4.4 × 10 ⁻⁴	-2.9 × 10 ⁻³	-3.5 × 10 ⁻³
	10 ⁻⁵ au	4.9 × 10 ⁻⁴	-4.7 × 10 ⁻⁴	-4.7 × 10 ⁻⁴	-1.9 × 10 ⁻³	-2.0 × 10 ⁻³
	10 ⁻⁶ au	2.4 × 10 ⁻⁴	-4.6 × 10 ⁻⁴	-4.6 × 10 ⁻⁴	-1.8 × 10 ⁻³	-1.9 × 10 ⁻³

^a ANO-L C, N, O [4s3p1d]/H[2s1p] with explicit molecule-centered [1s1p1d] Rydberg functions.**Table 4.** Absolute Mean Errors in eV for CASPT2 Excitation Energies as a Function of AO Basis Set, CD Threshold (in au), and CD Auxiliary Basis Set (without and with pruning)

basis set	CD-thres.	mean absolute error for CASPT2 calculations				
		full-CD	aCD	acCD	(SHAC)	
					aCD	acCD
TZVP	10 ⁻³ au	4.4 × 10 ⁻³	1.1 × 10 ⁻³	1.3 × 10 ⁻³	6.3 × 10 ⁻³	6.0 × 10 ⁻³
	10 ⁻⁴ au	8.4 × 10 ⁻⁴	6.1 × 10 ⁻⁴	6.1 × 10 ⁻⁴	7.2 × 10 ⁻⁴	7.7 × 10 ⁻⁴
	10 ⁻⁵ au	1.3 × 10 ⁻⁴	2.0 × 10 ⁻⁴	2.0 × 10 ⁻⁴	7.0 × 10 ⁻⁴	7.0 × 10 ⁻⁴
	10 ⁻⁶ au	1.7 × 10 ⁻⁵	2.0 × 10 ⁻⁴	2.1 × 10 ⁻⁴	7.0 × 10 ⁻⁴	7.0 × 10 ⁻⁴
ANO-RCC-VDZP	10 ⁻³ au	4.4 × 10 ⁻³	1.8 × 10 ⁻⁴	1.4 × 10 ⁻⁴	1.5 × 10 ⁻³	1.5 × 10 ⁻³
	10 ⁻⁴ au	3.3 × 10 ⁻⁴	1.9 × 10 ⁻⁴	1.8 × 10 ⁻⁴	1.4 × 10 ⁻³	1.5 × 10 ⁻³
	10 ⁻⁵ au	4.4 × 10 ⁻⁵	1.9 × 10 ⁻⁴	1.8 × 10 ⁻⁴	1.3 × 10 ⁻³	1.3 × 10 ⁻³
	10 ⁻⁶ au	5.9 × 10 ⁻⁶	1.8 × 10 ⁻⁴	1.8 × 10 ⁻⁴	1.2 × 10 ⁻³	1.2 × 10 ⁻³
ANO-RCC-VTZP	10 ⁻³ au	5.2 × 10 ⁻³	4.5 × 10 ⁻⁵	2.3 × 10 ⁻⁵	1.7 × 10 ⁻⁴	1.5 × 10 ⁻⁴
	10 ⁻⁴ au	2.4 × 10 ⁻⁴	3.5 × 10 ⁻⁵	1.4 × 10 ⁻⁵	1.6 × 10 ⁻⁴	1.5 × 10 ⁻⁴
	10 ⁻⁵ au	1.9 × 10 ⁻⁵	9.6 × 10 ⁻⁶	7.0 × 10 ⁻⁶	1.3 × 10 ⁻⁴	1.3 × 10 ⁻⁴
	10 ⁻⁶ au	1.0 × 10 ⁻⁵	2.9 × 10 ⁻⁶	2.5 × 10 ⁻⁶	1.2 × 10 ⁻⁴	1.2 × 10 ⁻⁴
ANO-RCC-VQZP	10 ⁻³ au	4.0 × 10 ⁻³	9.8 × 10 ⁻⁶	7.1 × 10 ⁻⁶	5.5 × 10 ⁻⁵	6.6 × 10 ⁻⁵
	10 ⁻⁴ au	5.5 × 10 ⁻⁴	6.6 × 10 ⁻⁷	2.0 × 10 ⁻⁶	2.2 × 10 ⁻⁵	6.5 × 10 ⁻⁵
	10 ⁻⁵ au	3.5 × 10 ⁻⁵	4.4 × 10 ⁻⁷	1.5 × 10 ⁻⁶	2.1 × 10 ⁻⁵	2.0 × 10 ⁻⁵
	10 ⁻⁶ au	4.8 × 10 ⁻⁶	5.1 × 10 ⁻⁷	3.4 × 10 ⁻⁷	1.9 × 10 ⁻⁵	1.9 × 10 ⁻⁵
ANO-L + Rydberg ^a	10 ⁻³ au	1.6 × 10 ⁻³	5.7 × 10 ⁻⁵	7.0 × 10 ⁻⁵	6.5 × 10 ⁻⁴	6.1 × 10 ⁻⁴
	10 ⁻⁴ au	1.5 × 10 ⁻⁴	5.9 × 10 ⁻⁵	6.1 × 10 ⁻⁵	6.0 × 10 ⁻⁴	6.8 × 10 ⁻⁴
	10 ⁻⁵ au	2.9 × 10 ⁻⁵	5.9 × 10 ⁻⁵	5.8 × 10 ⁻⁵	4.3 × 10 ⁻⁴	4.7 × 10 ⁻⁴
	10 ⁻⁶ au	8.6 × 10 ⁻⁶	5.8 × 10 ⁻⁵	5.7 × 10 ⁻⁵	4.4 × 10 ⁻⁴	4.4 × 10 ⁻⁴

^a ANO-L C, N, O [4s3p1d]/H[2s1p] with explicit molecule-centered [1s1p1d] Rydberg functions.

high angular momentum components contribute insignificantly to the energy in most cases, the higher angular components of the auxiliary basis set are eliminated. This pruning technique (SHAC), originally suggested by Eichkorn et al.,⁴⁶ was explored in our previous benchmark study.⁸ It was concluded that, although the pruning reduced the CD auxiliary basis set convergence toward an exact representation of the two-electron integrals, this was of no consequence in most quantum-chemical studies. While it was noted in the first benchmark study on total ground state energies⁸ that this technique indeed reduces the accuracy, the current investigation on CASPT2 and CASSCF excitation energies

exhibits a close to perfect cancellation of errors. This remarkable feature is demonstrated for all types of AO basis sets and for both valence and Rydberg excited states (see Figures 1–3). The conclusion is that, for excitation energies, acCD auxiliary basis sets with a CD threshold of 10⁻³ au introduce an error which is insignificant. With this procedure, standard deviations in the computed excitation energies are below 0.01 eV.

CASSCF vs CASPT2. It is well-known that the AO basis set convergence of the CASSCF method is significantly different from that of the CASPT2 method. While methods

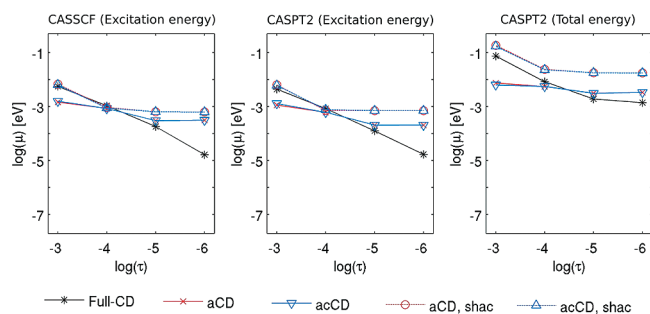


Figure 1. Mean absolute errors for excitation energies, μ , at the CASSCF (left panel) and CASPT2 (center panel) levels of theory, and mean absolute errors, μ , of the total energies at the CASPT2 level of theory (right panel) calculated with the TZVP basis set, with and without skipping of higher angular momenta (SHAC), as explained in section 3, plotted as a function of the CD threshold, τ .

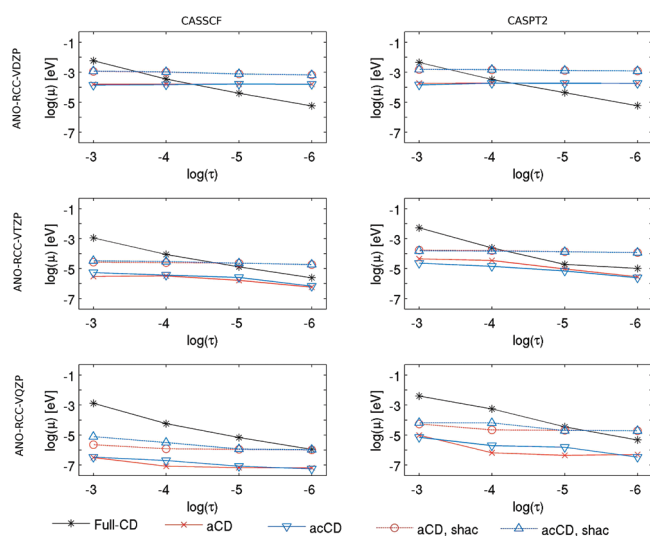


Figure 2. Mean absolute errors for excitation energies, μ , computed at the CASSCF (left) and CASPT2 (right) levels of theory with the ANO-RCC-VXZP, X = D, T, Q, basis sets, plotted as a function of the CD threshold, τ .

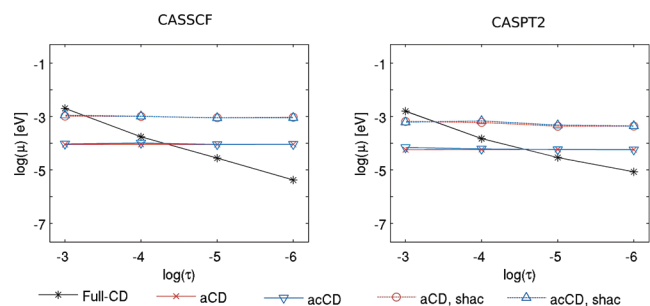


Figure 3. Mean absolute errors for excitation energies, μ , of Rydberg states at the CASSCF (left panel) and CASPT2 (right panel) levels of theory, with and without skipping of higher angular momenta (SHAC), plotted as a function of the CD threshold, τ .

like HF and CASSCF show close to AO basis set saturation already for triple- ζ quality AO basis sets, correlated methods like CASPT2 tend to need at least quadruple- ζ to achieve the same. Does this fact impact the requirements of the auxiliary basis sets? Looking at Figure 2 and comparing the

left and right panel columns, we note hardly any significant accuracy difference in the computed CASSCF and CASPT2 excitation energies, with the possible exception that there is a slightly lower accuracy for the CASPT2 vs the CASSCF excitation energies for the ANO-RCC-VQZP basis set.

Rydberg vs Valence States. The accuracy assessments related to the 72 Rydberg states are presented in Figure 3.

In this study, we have employed explicit Rydberg basis sets^{39–41} placed in the center of the molecule. This technique differs from that of adding atom-centered diffuse functions to the standard atomic AO basis sets, and its ability to accurately and conveniently reduce valence-Rydberg mixing and aid in identifying the Rydberg states has been documented previously.^{41,42} We note that in the paper of Bauernschmitt et al.³² the authors pointed out that the error in the computed Rydberg state excitation energies was larger, 0.08 eV, initially and that *ad hoc* decontraction or addition of diffuse auxiliary basis functions was required to achieve an accuracy similar to that of the errors found in the valence excitation energies, namely, 0.01 eV. In the full-CD, aCD, and acCD approaches, the explicit Rydberg AO basis does not require any special treatment as compared to any other AO basis set. Comparing Figure 3 with Figure 2 for the ANO-RCC-VTZP basis set, we note a slightly larger error in the case of the Rydberg excitations in combination with the aCD and acCD auxiliary basis sets. This is to some extent expected, considering the diffuse character of the explicit Rydberg basis and that these basis sets carry a lower significance in the aCD and acCD procedures. However, this can be completely ignored given that the mean absolute error in the excitation energies of the Rydberg states is on the order of 0.001 eV or better. For the full-CD approach, we find no significant error when comparing valence and Rydberg excitation energies. We conclude that, unlike the conventional DF auxiliary basis sets, no particular care has to be applied in the computation of Rydberg excitation energies for the present approaches.

Distribution of Errors. Finally, we analyze the distribution of errors and their maximum. A typical display of these is presented in Figure 4.

In particular, we note that the standard deviation in all cases, with the possible exception of full-CD with a CD threshold of 10^{-3} au, are below 0.01 eV. The same holds true for the maximum error. Furthermore, for thresholds tighter or equal to 10^{-4} au, standard deviations and maximum errors equal to or below 0.001 eV are observed. The accuracy here is certainly more than just in parity to assessments with external auxiliary basis sets^{32,33}

4. Timings

Finally, we conclude this calibration paper with some brief notes on a typical representative case of an improvement in timings due to the use of the CD approximation for the CASPT2/CASSCF procedure. For this purpose, we have chosen to report the performances on some of the CASPT2 calculations described in ref 47. These systems are important intermediates from the reaction of O_2 with a Cu(I)- α -ketocarboxylate, and the accurate evaluation of the singlet-triplet splitting in each species is essential to the understand-

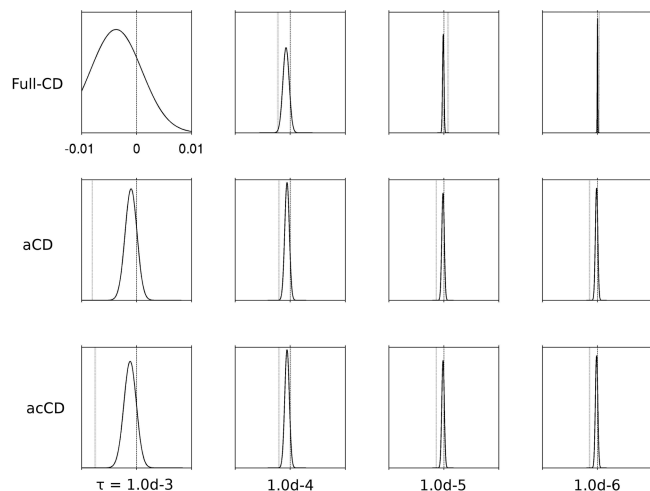


Figure 4. Display of the error distribution (in eV) as a function of the CD thresholds (in au) and DF approximations with the TZVP valence basis set. In this graph, the width of the Gaussian distribution is associated with the standard deviation. A dashed vertical line represents the maximum error found for the test set. The labeling of the upper left corner graph applies to all other graphs.

ing of the mechanism of activation of molecular oxygen by copper coordination complexes.¹⁹ As described in detail in the original publication,⁴⁷ Cholesky-based CASSCF/CASPT2 calculations were performed with a decomposition threshold of 10^{-5} using ANO basis sets of double- ζ quality. This corresponds to a range of about 280 to 450 contracted Gaussian basis functions, depending on the system (point group symmetry not employed). In this range, the time spent to generate the DF-vectors is nearly independent of the particular choice of the Cholesky basis (full-CD, aCD, etc.), and so are the subsequent steps. For the smallest calculation, the CASPT2 step alone requires a wall-time of about 2 h using conventional two-electron integrals, compared to the 1 h of the full-CD (10^{-5}) implementation. The timings refer to an architecture of the type Intel(R) Xeon(TM) 3.20 GHz with 8 GB RAM and are those for the (8in8) choice of the active space (nearly identical timings result from the singlet or triplet calculation). Noticeably, the generation of the two-electron integrals in the MO basis shows alone a much better ratio: 85 vs 4885 s in wall-time (a factor 10 in CPU time). As discussed in the implementation paper,¹⁴ the present DF-CASPT2 algorithm differs from the conventional only in the generation of the two-electron integrals in MO basis, whereas other computationally heavy tasks are left unchanged. In the above example, the task of solving the equations for the first-order wave function requires roughly 1 h of wall-time (45 min CPU time), and that explains why the resulting speedup is only a factor two. Moving toward the upper limit of 450 basis functions for our systems, the conventional calculations can hardly be afforded due to the large disk-space requirements. When possible, the DF-CASPT2 alone outperforms the conventional implementation by a factor of 5–8 in wall-time and with effectively no loss of accuracy (computed S–T splittings within 0.1 kcal/mol from conventional results). It should be also pointed out that the preliminary DF-CASSCF calculation can be performed at much lower costs than

conventional calculations, and if included in the counting together with the integral/DF-vector generation, it gives rise to overall speedups that are much larger—not uncommonly 1–2 orders of magnitude. As an example, the generation of the Cholesky vectors for the smallest system requires only 5 min of wall-time, compared to 39 min needed to compute/store the AO two-electron integrals. The DF-CASSCF step is in this case about 4 times faster, 6 vs 25 min of wall-time.

5. Summary

In this study, we have reported the first accuracy assessments of the CD auxiliary basis set in association with the evaluation of vertical valence and Rydberg excitation energies computed with the CASSCF/CASPT2 protocol. These assessments clearly demonstrate the accuracy and flexibility of the CD auxiliary basis sets, specifically: (i) CD auxiliary basis sets offer excellent cancellation of errors. (ii) No significant differences were detected in comparing the errors associated with different AO basis sets. (iii) CD auxiliary basis set pruning can be employed safely. (iv) CD auxiliary basis sets give rise to essentially the same (insignificant) error in conjunction with CASSCF and CASPT2 excitation energy calculations. (v) The use of the CD procedure can reduce CASPT2/CASSCF wall-time by a factor of 4 up to 1–2 orders of magnitude. (vi) No special treatment of the CD auxiliary basis set is required in the computation of Rydberg excitation energies. (vii) The standard deviation observed by using the CD auxiliary basis sets in the computation of vertical excitation energies is well below 0.01 eV. (viii) CD threshold as high as 10^{-3} au can be used for calculating vertical valence and Rydberg excitation energies, giving mean and maximum errors in the range of 0.01 eV, and finally, (ix) for tighter thresholds, the CD auxiliary basis sets induce errors that are virtually completely insignificant.

Acknowledgment. The authors thank the Swedish Research Council (VR), the CoE Centre for Theoretical and Computational Chemistry (179568/V30), projects CTQ2007-61260 and CSD2007-0010 Consolider-Ingenio in Molecular Nanoscience of the Spanish MICINN/FEDER, and the Swedish Research Council (VR) through the Linnaeus Center of Excellence on Organizing Molecular Matter (OMM) for financial support.

Supporting Information Available: Tables 5–8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Aquilante, F.; Lindh, R.; Pedersen, T. B. *J. Chem. Phys.* **2007**, *127*, 114107.
- (2) Aquilante, F.; Lindh, R.; Pedersen, T. B. *J. Chem. Phys.* **2008**, *129*, 034106.
- (3) Pedersen, T. B.; Aquilante, F.; Lindh, R. *Theor. Chem. Acc.* **2009**, *124*, 1–10.
- (4) Aquilante, F.; Gagliardi, L.; Pedersen, T. B.; Lindh, R. *J. Chem. Phys.* **2009**, *130*, 154107.
- (5) Beebe, N. H. F.; Linderberg, J. *Int. J. Quantum Chem.* **1977**, *12*, 683–705.

- (6) Koch, H.; Sanchez de Meras, A.; Pedersen, T. B. *J. Chem. Phys.* **2003**, *118*, 9481–9484.
- (7) Weigend, F.; Kattannek, M.; Ahlrichs, R. *J. Chem. Phys.* **2009**, *130*, 164106.
- (8) Boström, J.; Aquilante, F.; Pedersen, T. B.; Lindh, R. *J. Chem. Theory Comput.* **2009**, *5*, 1545–1553.
- (9) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.
- (10) Roos, B. O. *Int. J. Quantum Chem.* **1980**, *S14*, 175–189.
- (11) Aquilante, F.; Pedersen, T. B.; Lindh, R.; Roos, B. O.; Sánchez de Merás, A.; Koch, H. *J. Chem. Phys.* **2008**, *129*, 024113.
- (12) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483–5488.
- (13) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218–1226.
- (14) Aquilante, F.; Malmqvist, P.-Å.; Pedersen, T. B.; Ghosh, A.; Roos, B. O. *J. Chem. Theory Comput.* **2008**, *4*, 694.
- (15) Schreiber, M.; Silva-Junior, M. R.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *128*, 134110.
- (16) Silva-Junior, M. R.; Schreiber, M.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *129*, 104103.
- (17) Pierloot, K.; Vancoillie, S. *J. Chem. Phys.* **2008**, *128*, 034104.
- (18) Radon, M.; Pierloot, K. *J. Phys. Chem. A* **2008**, *112*, 11824–11832.
- (19) Huber, S. M.; Ertem, M. Z.; Aquilante, F.; Gagliardi, L.; Tolman, W. B.; Cramer, C. J. *Chem.—Eur. J.* **2009**, *15*, 4886–4895.
- (20) Hättig, C.; Weigend, F. *J. Chem. Phys.* **2000**, *113*, 5154–5161.
- (21) Hättig, C.; Köhn, A. *J. Chem. Phys.* **2002**, *117*, 6939–6951.
- (22) Hättig, C.; Hald, K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2111–2118.
- (23) Kähn, A.; Hättig, C. *J. Chem. Phys.* **2003**, *119*, 5021–5036.
- (24) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *243*, 409–418.
- (25) Pedersen, T. B.; Sanchez de Meras, A. M. J.; Koch, H. *J. Chem. Phys.* **2004**, *120*, 8887–8897.
- (26) Pedersen, T. B.; Koch, H.; Boman, L.; Sánchez de Merás, A. M. J. *Chem. Phys. Lett.* **2004**, *393*, 319–326.
- (27) García Cuesta, I.; Pedersen, T. B.; Koch, H.; Sánchez de Merás, A. *Chem. Phys. Lett.* **2004**, *390*, 170–175.
- (28) García Cuesta, I.; Sanchez Marín, J.; Pedersen, T. B.; Koch, H.; Sanchez de Meras, A. M. J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 361–365.
- (29) Pedersen, T. B.; Kongsted, J.; Crawford, T. D.; Ruud, K. *J. Chem. Phys.* **2009**, *130*, 034310.
- (30) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.
- (31) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (32) Bauernschmitt, R.; Häser, M.; Treutler, O.; Ahlrichs, R. *Chem. Phys. Lett.* **1997**, *264*, 573–578.
- (33) Rappoport, D.; Furche, F. *J. Chem. Phys.* **2005**, *122*, 064105.
- (34) Neese, F.; Olbrich, G. *Chem. Phys. Lett.* **2002**, *362*, 170–178.
- (35) Grimme, S.; Neese, F. *J. Chem. Phys.* **2007**, *127*, 154116.
- (36) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
- (37) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291–306.
- (38) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2004**, *108*, 2851–2858.
- (39) Serrano-Andrés, L.; Merchán, M.; Nebot-Gil, I.; Lindh, R.; Roos, B. O. *J. Chem. Phys.* **1993**, *98*, 3151–3162.
- (40) Serrano-Andrés, L.; Fülischer, M. P. *J. Am. Chem. Soc.* **1996**, *118*, 12190–12199.
- (41) Roos, B. O. The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations. In *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry - II*; Lawley, K. P., Ed.; John Wiley & Sons Ltd.: Chichester, England, 1987; Chapter 69, p 399.
- (42) Finley, J.; Malmqvist, P.-Å.; Roos, B. O.; Serrano-Andrés, L. *Chem. Phys. Lett.* **1998**, *288*, 299–306.
- (43) Forsberg, N.; Malmqvist, P.-Å. *Chem. Phys. Lett.* **1997**, *274*, 196.
- (44) Ghigo, G.; Roos, B. O.; Malmqvist, P.-Å. *Chem. Phys. Lett.* **2004**, *396*, 142–149.
- (45) (a) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimelpfennig, B.; Neogady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222–239. (b) Veryazov, V.; Widmark, P.-O.; Serrano-Andrés, L.; Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **2004**, *100*, 626–653. (c) Aquilante, F.; De Vico, L.; Ferre, N.; Ghigo, G.; Malmqvist, P.-Å.; Neogady, P.; Pedersen, T. B.; Pitonak, M.; Reiher, M.; Roos, B. O.; Serrano-Andrés, L.; Urban, M.; Veryazov, V.; Lindh, R. *J. Comput. Chem.* **2010**, *31*, 224–247.
- (46) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119–124.
- (47) Huber, S. M.; Shahi, A. R. M.; Aquilante, F.; Cramer, C. J.; Gagliardi, L. *J. Chem. Theory Comput.* **2009**, *5*, 2967.

CT900612K