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Accuracy of geometries: influence of basis set, exchange–correlation potential, inclusion of core electrons, and relativistic corrections

M. Swart[1,2], **J.G. Snijders**[1]

[1] Theoretische Chemie (MSC), Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[2] Organische en Anorganische Chemie, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract. The geometries of a set of small molecules were optimized using eight different exchange–correlation (xc) potentials in a few different basis sets of Slater-type orbitals, ranging from a minimal basis (I) to a triple-zeta valence basis plus double polarization functions (VII). This enables a comparison of the accuracy of the xc potentials in a certain basis set, which can be related to the accuracies of wavefunction-based methods such as Hartree–Fock and coupled cluster. Four different checks are done on the accuracy by looking at the mean error, standard deviation, mean absolute error and maximum error. It is shown that the mean absolute error decreases with increasing basis set size, and reaches a basis set limit at basis VI. With this basis set, the mean absolute errors of the xc potentials are of the order of 0.7–1.3 pm. This is comparable to the accuracy obtained with CCSD and MP2/MP3 methods, but is still larger than the accuracy of the CCSD(T) method (0.2 pm). The best performing xc potentials are found to be Becke–Perdew, PBE and PW91, which perform as well as the hybrid B3LYP potential. In the second part of this paper, we report the optimization of the geometries of five metallocenes with the same potentials and basis sets, either in a nonrelativistic or a scalar relativistic calculation using the zeroth-order regular approximation approach. For the first-row transition-metal complexes, the relativistic corrections have a negligible effect on the optimized structures, but for ruthenocene they improve the optimized Ru–ring distance by some 1.4–2.2 pm. In the largest basis set used, the absolute mean error is again of the order of 1.0 pm. As the wavefunction-based methods either give a poor performance for metallocenes (Hartree–Fock, MP2), or the size of the system makes a treatment with accurate methods such as CCSD(T) in a reasonable basis set cumbersome, the good performance of density functional theory calculations for these molecules is very promising; even more so as density functional theory is an efficient method that can be used without problems on systems of this size, or larger.

Keywords: Quantum chemistry – Geometry optimization – Basis set – Density functional theory

Introduction

Before one can perform a quantum chemical calculation, one needs to have a structure of the molecule; for example, one needs to know where the atoms are positioned in space (its geometry). The accuracy with which these geometries can be predicted by different quantum chemical methods is a very useful thing to know, allowing an estimate of the reliability of a computed geometry.

In two recent papers, Helgaker and coworkers [1, 2] presented a systematic investigation of the accuracy obtainable with wavefunction-based methods, applying a hierarchy of basis sets and methods on a set of 19 small closed-shell molecules.[1] They used Hartree–Fock (HF), configuration interaction (CISD), Møller–Plesset (MP2, MP3, MP4) and coupled-cluster methods [CCSD, CCSD(T)] in Dunning's correlation-consistent basis sets (cc-pVDZ, cc-pVTZ, cc-pVQZ) [3], and looked at the mean error, standard deviation, mean absolute error and maximum error. HF is shown to result always in a too short bond distance, while the inclusion of the electron correlation tends to increase it. Increasing the basis set size tends to decrease the bond distance again. The best results are obtained when one uses the CCSD(T) method, either in the cc-pVTZ or the cc-pVQZ basis, with an accuracy (0.22 pm) that is comparable to the

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Correspondence to: M. Swart
e-mail: swart@chem.vu.nl

[1] The set of small molecules consists of: HF, H_2O, NH_3, CH_4, N_2, CH_2, CO, HCN, CO_2, HNC, C_2H_2, CH_2O, HNO, N_2H_2, O_3, C_2H_4, F_2, HOF, H_2O_2

Table 1. ADF basis set description

	I	II	III	IV	V	VI	VII
H	S^1	S^2	S^2P^1	S^3P^1	$S^3P^1D^1$	$S^4P^2D^1$	$S^6P^3D^2$
C	S^2P^1	S^4P^2	$S^4P^2D^1$	$S^5P^3D^1$	$S^5P^3D^1F^1$	$S^6P^4D^2F^1$	$S^8P^6D^3F^2$
C1*s*[a]	S^2P^1/S^1	S^3P^2/S^1	$S^3P^2D^1/S^1$	$S^4P^3D^1/S^1$	$S^4P^3D^1F^1/S^1$	–	–
Fe	$S^3P^3D^1$	$S^8P^5D^3$	–	$S^9P^5D^3$	–	$S^{11}P^7D^5F^1$	–
Fe2*p*[a]	–	$S^6P^4D^3/S^2P^1$	–	$S^7P^4D^3/S^2P^1$	–	–	–

[a] X/Y:X are the valence basis functions, Y the orthogonal core functions

experimental uncertainty. In another paper, Koch et al. [4] investigated the molecular structure of ferrocene with the same methods, and found again good agreement with the experimental structure.

In this study, a similar systematic investigation is presented where the accuracy of geometries as predicted by density functional theory (DFT) is studied. The influence of the basis set, treatment of core electrons and relativistic corrections has been investigated for several currently available exchange–correlation (xc) potentials. The same set of 19 small molecules is used in the first part, to enable not only a comparison with experimental data but also with the wavefunction-based results obtained by Helgaker and coworkers. For these molecules, the influence of including the core electrons in the optimizations has been investigated. Although some studies [5, 6, 7, 8] have already focused on the accuracy of geometries by some xc potentials, a systematic investigation of this kind has not been reported before (to the best of our knowledge). This is most certainly the case for the Slater-type basis sets used in ADF, as well as for the comparison with the study by Helgaker and coworkers.

Besides this set of molecules, a set of metallocene molecules was also used, where not only the inclusion of core electrons was investigated, but also the effect of scalar relativistic corrections (with the zeroth-order regular approximation, ZORA, [9, 10] Hamiltonian).[2] All of these calculations were performed in the standard available basis sets, ranging from a single-zeta valence basis set (SZV, I) to a triple-zeta valence basis set plus double polarization functions (TZ2P, VII). As B3LYP [11] is not a pure DFT potential, and needs a portion of HF exchange, it can not be used in the ADF program. To check the accuracy of it, as well as to compare the ADF basis sets to the basis sets used in the work of Helgaker et al. [1], the geometry optimizations were also performed with the B3LYP and BLYP potentials in the cc-pVDZ and cc-pVTZ basis sets using the HONDO98 [12, 13] program.

Computational details

In the ADF program [9, 14], standard basis sets are available ranging from small (SZV, I) to large (TZ2P, VII), with for the basis sets up to TZ2P (V) the option of either including (all electron) or excluding (frozen core) the core electrons explicitly in the calculations. In the frozen-core basis sets, there are still basis functions assigned to the core electrons; the basis functions of the valence electrons are then explicitly orthogonalized to them. As the calculations are significantly faster when the core electrons are not included, this is normally the preferred option. For clarity and the sake of completeness, a short description of the basis sets is given in Table 1, for hydrogen, carbon and iron.

The following standard available pure xc potentials were examined: local density approximation (LDA), Becke88 exchange [15] combined with Perdew86 correlation [16] (Becke–Perdew), BLAP3 [17], Becke88 exchange [15] with Lee–Young–Parr correlation [18] (BLYP), Perdew–Burke–Ernzerhof (PBE) [19], Perdew–Wang (PW91) [20, 21], revised Perdew–Burke–Ernzerhof (REVPBE) [22] and RPBE [23].

To compare the basis sets, the cc-pVDZ and cc-pVTZ basis sets were used also for the BLYP potential using HONDO98. Moreover, the B3LYP potential was also used with this program in the same basis sets to enable a rough comparison with the pure DFT xc potentials.

Scalar relativistic corrections can be included in the calculations quite easily in ADF, using the ZORA approach [9, 10], which is generally found to give an accurate description of the relativistic effects. Although spin–orbit coupling is possible also with the ZORA approach, this effect was not included since the gradients are not implemented yet; therefore it is not possible to optimize the geometries directly.

Several statistical measures were used to quantify the accuracy of the methods. The difference between the calculated, R_i^{calc}, and experimental, R_i^{exp}, bond length gives the error, Δ_i:

$$\Delta_i = R_i^{\mathrm{calc}} - R_i^{\mathrm{exp}} \quad . \tag{1}$$

For each basis set (if possible, both with and without including the core electrons explicitly) and xc potential, the mean error, $\bar{\Delta}$, the standard deviation in the errors, Δ_{std}, the mean absolute error, $\bar{\Delta}_{\mathrm{abs}}$, and the maximum error, Δ_{max}, were calculated:

$$\begin{aligned} \bar{\Delta} &= \frac{1}{n}\sum_{i=1}^{n} \Delta_i \\ \Delta_{\mathrm{std}} &= \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} \left(\Delta_i - \bar{\Delta}\right)^2} \; , \\ \bar{\Delta}_{\mathrm{abs}} &= \frac{1}{n}\sum_{i=1}^{n} |\Delta_i|, \\ \Delta_{\mathrm{max}} &= \max|\Delta_i| \quad . \end{aligned} \tag{2}$$

Each measure characterizes a specific aspect of the performance of the xc potentials and basis sets. The two first measures characterize the distribution of errors about a mean value $\bar{\Delta}$ for a given xc potential in a certain basis set, thus quantifying both systematic and nonsystematic errors. The mean absolute error represents the typical magnitude of the errors in the calculations, while the maximum error indicates how large the errors can be.

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[2] The metallocene set: manganocene, ferrocene, cobaltocene, nickelocene and ruthenocene

Table 2. Experimental bond lengths (picometers; taken from Ref. [1])

Molecule	Bond	Bond length	Molecule	Bond	Bond length
C_2H_2	CH	106.2	HCN	CH	106.5
C_2H_2	CC	120.3	HCN	CN	115.3
C_2H_4	CH	108.1	HF	HF	91.7
C_2H_4	CC	133.4	HNC	NH	99.4
CH_2	CH	110.7	HNC	CN	116.9
CH_2O	CH	109.9	HNO	NH	106.3
CH_2O	CO	120.3	HNO	NO	121.2
CH_4	CH	108.6	HOF	OH	96.6
CO	CO	112.8	HOF	OF	143.5
CO_2	CO	116.0	N_2	NN	109.8
F_2	FF	141.2	N_2H_2	NH	102.8
H_2O	OH	95.7	N_2H_2	NN	125.2
H_2O_2	OH	96.7	NH_3	NH	101.2
H_2O_2	OO	145.6	O_3	OO	127.2

Small molecules

The experimental values for the bond lengths of the set of small molecules are given in Table 2, but before reporting the statistical results for all small molecules, it may be instructive to report the optimized bond length for one particular molecule (N_2 in this case) for all different xc potentials and basis sets (Table 3). A general improvement with increasing basis set size is observed.

The mean errors for the eight xc potentials in basis sets I–VII are given in Table 4, both in an all-electron and a frozen-core basis if available. In all cases, the bond lengths are on average overestimated, with an improvement of the results as the basis set size is increased. For the frozen-core basis sets, the average of the mean errors for the eight xc potentials improves gradually from 5.63 pm in basis I to 0.92 pm in basis set V. The same trend is observed for the all-electron basis sets, which show still an improvement on going from basis set V to VI of some 0.2 pm. However, going from basis set VI to VII, no further improvement is observed, which seems to indicate that the basis set limit has been reached (at least concerning the accuracy of geometries). The difference between the all-electron and frozen-core basis sets is quite small; the all-electron basis sets seem to perform slightly better in the smaller basis sets, while the frozen-core basis set seems to give slightly better results in basis sets IV and V.

Table 3. Deviation (pm) of the optimized N_2bond length from the experimental value of 109.77 pm

Exchange–correlation potential	I	II	III	IV	V	VI	VII
Frozen core							
Becke–Perdew	+10.52	+2.19	+0.75	+0.72	+0.40	–	–
BLAP3	+10.99	+2.18	+0.73	+0.68	+0.33	–	–
BLYP	+10.90	+2.36	+0.90	+0.82	+0.48	–	–
LDA	+9.88	+1.42	+0.13	+0.02	–0.27	–	–
PBE	+10.42	+2.17	+0.74	+0.75	+0.44	–	–
PW91	+10.43	+2.01	+0.60	+0.59	+0.27	–	–
REVPBE	+10.54	+2.43	+0.96	+1.03	+0.71	–	–
RPBE	+10.58	+2.54	+1.05	+1.13	+0.81	–	–
All electron							
Becke–Perdew	+10.42	+2.18	+0.79	+0.79	+0.46	+0.39	+0.42
BLAP3	+10.86	+2.18	+0.78	+0.75	+0.38	+0.29	+0.32
BLYP	+10.78	+2.34	+0.94	+0.88	+0.53	+0.42	+0.45
LDA	+9.73	+1.36	+0.11	+0.04	–0.26	–0.33	–0.29
PBE	+10.32	+2.15	+0.77	+0.82	+0.49	+0.42	+0.44
PW91	+10.31	+2.00	+0.63	+0.64	+0.32	+0.24	+0.27
REVPBE	+10.51	+2.44	+1.01	+1.10	+0.78	+0.71	+0.73
RPBE	+10.55	+2.54	+1.09	+1.20	+0.87	+0.80	+0.81

Table 4. Mean errors (pm)

Exchange–correlation potential	I	II	III	IV	V	VI	VII
Frozen core							
Becke–Perdew	5.58	4.00	1.49	1.24	0.90	–	–
BLAP3	6.27	4.16	1.63	1.38	1.02	–	–
BLYP	6.09	4.32	1.82	1.55	1.21	–	–
LDA	4.65	3.26	0.83	0.61	0.28	–	–
PBE	5.44	3.97	1.43	1.19	0.87	–	–
PW91	5.47	3.81	1.31	1.08	0.74	–	–
REVPBE	5.75	4.28	1.68	1.45	1.13	–	–
RPBE	5.76	4.36	1.76	1.54	1.21	–	–
Average	5.63	4.02	1.49	1.26	0.92	–	–
All electron							
Becke–Perdew	5.54	3.96	1.44	1.30	0.98	0.81	0.82
BLAP3	6.20	4.09	1.58	1.44	1.09	0.92	0.91
BLYP	6.00	4.24	1.76	1.61	1.26	1.09	1.08
LDA	4.55	3.16	0.74	0.62	0.31	0.17	0.17
PBE	5.36	3.93	1.37	1.29	0.93	0.78	0.78
PW91	5.38	3.76	1.25	1.14	0.82	0.66	0.65
REVPBE	5.65	4.23	1.66	1.52	1.20	1.04	1.04
RPBE	5.76	4.33	1.74	1.61	1.28	1.12	1.12
Average	5.56	3.96	1.44	1.32	0.98	0.82	0.82

When looking at the mean errors, the LDA seems to give the best performance, with a mean error, for instance, in basis sets VI and VII of only 0.17 pm. This value is of the same order of magnitude as was found for CCSD(T). The other xc potentials are less accurate (about 0.6–1.1 pm), but still give results comparable with CCSD in the largest basis set. The worst results are obtained with the BLYP, REVPBE and RPBE potentials, which are the only ones that still give a mean error that is larger than 1 pm in the largest basis set.

The standard deviations in the mean errors is given in Table 5, and show the same improving trend on increasing the basis set size. Also here the frozen-core and all-electron basis sets perform equally well. There are some small differences, but not as large as the ones observed between basis sets of different size, i.e., whereas the former differences are of the order of 0.1 pm (comparing, for instance, Becke–Perdew in basis set IV), the latter are a few times larger (comparing, for instance, the frozen-core Becke–Perdew results in basis sets III and IV, respectively). The LDA no longer performs best in this respect. Although it had the smallest mean error of all potentials, the standard deviation belonging to it is the largest (about 1.5 pm in basis sets V–VII) of all the xc potentials in the larger basis sets; in the medium basis sets, also a large standard deviation is found for the BLAP3 potential. In fact, for the larger basis sets, all

Table 5. Standard deviations (pm)

Exchange–correlation potential	I	II	III	IV	V	VI	VII
Frozen core							
Becke–Perdew	3.47	3.80	0.94	0.61	0.59	–	–
BLAP3	3.51	4.64	1.64	1.35	1.13	–	–
BLYP	3.55	4.32	1.38	1.09	0.89	–	–
LDA	3.59	2.85	1.28	1.21	1.46	–	–
PBE	3.55	3.75	0.89	0.56	0.60	–	–
PW91	3.45	3.76	0.92	0.57	0.56	–	–
REVPBE	3.49	4.03	0.97	0.61	0.53	–	–
RPBE	3.35	4.07	1.00	0.65	0.52	–	–
Average	3.50	3.90	1.13	0.83	0.79	–	–
All electron							
Becke–Perdew	3.43	3.92	1.00	0.63	0.58	0.59	0.59
BLAP3	3.48	4.74	1.86	1.45	1.21	1.06	1.09
BLYP	3.53	4.40	1.55	1.16	0.95	0.83	0.85
LDA	3.56	2.94	1.04	1.17	1.39	1.53	1.50
PBE	3.55	3.88	0.92	0.63	0.57	0.61	0.61
PW91	3.44	3.87	0.96	0.62	0.57	0.57	0.58
REVPBE	3.33	4.15	1.11	0.67	0.55	0.53	0.53
RPBE	3.39	4.22	1.16	0.71	0.55	0.51	0.53
Average	3.46	4.02	1.20	0.88	0.80	0.78	0.79

potentials give more or less equal standard deviations except three: BLAP3, BLYP and LDA. As BLYP was also one of the worst potentials in the case of mean errors, it seems that it cannot be used with great confidence for obtaining accurate geometries.

The mean absolute errors are given in Table 6. Just like the mean errors and the standard deviations, they are shown to improve gradually with increasing basis set size. Again there is hardly any difference between the results from either a frozen-core or an all-electron basis set; the difference between the averages of the frozen core and the all electron in basis set IV is for instance 0.06 pm, while the difference between the averages between basis sets III and IV for the frozen core is 0.23 pm. The results of basis set V are still improved on going to VI, but increasing the basis set even more (VII) does not improve them any more. So, where the accuracy of geometries is concerned, the basis set limit seems to be reached already in basis set VI.

Becke–Perdew, PBE and PW91 are found to be the best xc potentials, as they are the only ones that consistently give better results than the average for all basis sets, both in the frozen-core and in the all-electron basis sets. The mean absolute error in the basis set limit of 0.89 pm (Becke-Perdew), 0.86 pm (PBE) and 0.75 pm (PW91), are comparable to or slightly better than CCSD results (0.89 pm) in the largest basis set used by Helgaker et al. (cc-pVQZ). However, these deviations are still larger than the accuracy of the CCSD(T) method (0.1–0.2 pm), which may surpass even experimental accuracies. Although the LDA performed best for the mean error, in this case it performed the worst, with an average error of about 1.3 pm in the larger basis sets. In fact, for the all-electron basis sets, the LDA does not improve upon increasing the basis set size after basis set III.

The maximum errors for the xc potentials in a certain (frozen-core/all-electron) basis set are given in Table 7. These results do not show the gradual improvement as the basis set is increased; for instance, going from basis I to basis II the average maximum error increases from 10.7 to 13.4 pm; however, after increasing the basis set even more, it decreases again gradually, except for the LDA, which exhibits an oscillatory pattern. As the difference between basis sets VI and VII is small, these results also show that the basis set limit has been reached.

The difference between the frozen-core and all-electron basis sets is not negligible for the maximum error, at least not for the small and medium-sized basis sets. For basis set V, the difference is negligible again for

Table 6. Mean absolute errors (pm)

Exchange–correlation potential	I	II	III	IV	V	VI	VII
Frozen core							
Becke–Perdew	5.68	4.00	1.51	1.24	0.93	–	–
BLAP3	6.27	4.17	1.64	1.38	1.03	–	–
BLYP	6.13	4.32	1.82	1.55	1.21	–	–
LDA	5.05	3.28	1.21	1.14	1.28	–	–
PBE	5.61	3.97	1.45	1.20	0.92	–	–
PW91	5.57	3.82	1.34	1.09	0.80	–	–
REVPBE	5.87	4.28	1.68	1.45	1.13	–	–
RPBE	5.78	4.36	1.76	1.54	1.21	–	–
Average	5.75	4.03	1.55	1.32	1.06	–	–
All electron							
Becke–Perdew	5.64	3.98	1.45	1.30	1.00	0.88	0.89
BLAP3	6.20	4.13	1.59	1.44	1.09	0.93	0.93
BLYP	6.06	4.26	1.76	1.61	1.26	1.09	1.09
LDA	4.97	3.20	1.00	1.11	1.24	1.31	1.29
PBE	5.55	3.95	1.38	1.29	0.97	0.86	0.86
PW91	5.49	3.79	1.27	1.15	0.87	0.76	0.75
REVPBE	5.68	4.25	1.66	1.52	1.20	1.05	1.05
RPBE	5.78	4.35	1.74	1.61	1.28	1.12	1.12
Average	5.67	3.99	1.48	1.38	1.11	1.00	1.00

Table 7. Maximum errors (pm)

Exchange–correlation potential	I	II	III	IV	V	VI	VII
Frozen core							
Becke–Perdew	10.52	13.16	3.35	2.51	1.81	–	–
BLAP3	11.96	15.61	6.15	5.44	4.68	–	–
BLYP	11.32	14.91	5.43	4.73	3.95	–	–
LDA	9.88	9.69	3.30	2.32	2.85	–	–
PBE	10.42	12.97	3.31	2.11	1.85	–	–
PW91	10.43	12.83	3.23	2.13	1.64	–	–
REVPBE	10.60	13.90	3.89	2.96	2.11	–	–
RPBE	10.58	14.19	4.21	3.25	2.40	–	–
Average	10.71	13.41	4.11	3.18	2.66	–	–
All electron							
Becke–Perdew	10.42	13.42	3.98	2.68	1.82	1.75	1.75
BLAP3	11.82	15.88	6.72	5.36	4.66	4.10	4.18
BLYP	11.19	15.14	5.91	4.66	3.93	3.38	3.44
LDA	9.73	9.89	2.73	2.29	2.26	2.75	2.72
PBE	10.32	13.25	3.56	2.57	1.86	1.80	1.79
PW91	10.31	13.12	3.54	2.41	1.75	1.59	1.57
REVPBE	10.51	14.23	4.69	3.31	2.37	1.89	1.87
RPBE	10.73	14.53	5.03	3.63	2.49	2.00	2.22
Average	10.63	13.68	4.52	3.36	2.64	2.41	2.44

some potentials (e.g. Becke–Perdew, BLAP3 or PBE), while for others (LDA, REVPBE) there exists a large difference.

As was found for the mean absolute errors, there are three potentials (Becke–Perdew, PBE and PW91) that consistently give better results than the average for a certain basis set. For these three, the maximum error in the basis set limit (1.75, 1.79 and 1.57 pm, respectively, which was observed for the CH bond of CH_2O) is comparable to MP2 (1.67 pm) and MP4 (1.48 pm) in the largest basis set studied by Helgaker et al., and is substantially better than the CCSD method in the same basis (3.07 pm). Again, the accuracy of the CCSD(T) method (with a maximum error of 1.20 pm) is better than that of the best xc potentials.

Comparison with Dunning's basis set and the B3LYP potential

The results obtained with Dunning's basis sets for either the BLYP or the B3LYP potential are given in Table 8. Comparing the BLYP results in the cc-pVDZ basis set (e.g. [$s^3p^2d^1$] for carbon) with its ADF counterpart (III [$s^4p^2d^1$]), the mean absolute error of cc-pVDZ is slightly larger than basis set III; however, the maximum error is much smaller for cc-pVDZ than for basis III. The same inconsistencies show up for the mean error and its standard deviation; although the mean error is more or less comparable (1.76 for cc-pVDZ versus 1.81 pm for III), the standard deviations are quite different (1.06 for cc-pVDZ versus 1.55 pm for III). Therefore, as BLYP does not perform equally well in the cc-pVDZ and the ADF-III basis set, the B3LYP results (in the cc-pVDZ basis) cannot be compared directly with the pure xc potentials in basis III.

The size of the cc-pVTZ basis set ([4s3p2d1f] for carbon) is more or less between that of basis sets V ([5s3p1d1f]) and VI ([6s4p2d1f]) of ADF. This is reflected in the mean absolute error of the BLYP potential in the cc-pVTZ basis set (1.14 pm), which is somewhere between the results for basis sets V (1.26 pm) and VI (1.09 pm). Also the maximum error shows this trend: 3.55 pm (cc-pVTZ), 3.93 pm (V), 3.38 pm (VI). There is, however, a difference for the mean error, which is 0.98 pm in the cc-pVTZ basis, but slightly larger in the ADF basis sets (1.26 and 1.09 pm for basis sets V and VI, respectively); the standard deviation on the other hand is slightly lower in the ADF basis sets: 0.95 pm (V) and 0.83 pm (VI) versus 0.99 pm (cc-pVTZ). However, roughly speaking, the cc-pVTZ results for BLYP are similar to those in basis sets V and VI, which enables a comparison of B3LYP with the pure DFT potentials in ADF.

The mean error of B3LYP in the cc-pVTZ basis is almost zero (0.05 pm); however, the standard deviation is almost twice as large as those of Becke–Perdew or PW91. The mean absolute error is either comparable (PW91) or slightly better (Becke–Perdew, PBE) for the B3LYP potential. Finally, the maximum error is slightly larger for B3LYP compared with either Becke–Perdew, PBE or PW91. As a whole, B3LYP performs as well as the most accurate pure DFT potentials (Becke–Perdew, PBE, PW91), although with a slightly increased maximum error and standard deviation of the mean error.

Metallocenes

Metallocenes are molecules where a metal atom is sandwiched between two cyclopentadiene rings, which can exist in two conformations: staggered or eclipsed (Fig. 1).

The best known example of these metallocenes is ferrocene, which has been studied in great detail in the past by theoretical methods, and has been shown to be a difficult molecule for which an accurate prediction of the metal–ring distance could be obtained. Early HF calculations reported an Fe–ring distance of 188 pm, which is in poor agreement with the experimental distance of 166 pm. This could not be improved by employing larger basis sets, as it was established [24] that the HF limit is only slightly better than the early HF calculation (187.2 pm). Normally, such a poor performance could be improved upon by using MP2 calculations; for instance, the systematic study by Helgaker et al. (described earlier in this paper) showed a mean absolute error of 13.0 pm for HF, and only 2.4 pm for MP2. However, MP2 results for ferrocene [24] show a similarly dramatic

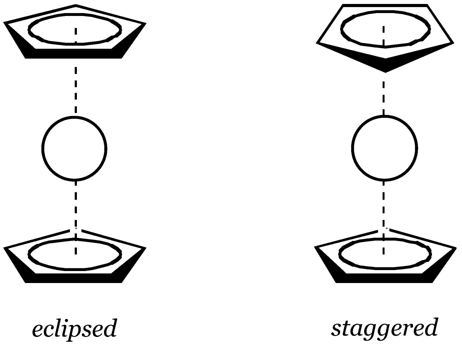

Fig. 1. Structure of metallocenes

Table 8. BLYP and B3LYP results (pm) in Dunning's basis sets

	BLYP cc-pVDZ	B3LYP cc-pVDZ	BLYP cc-pVTZ	B3LYP cc-pVTZ
Mean error	1.81	0.98	0.66	0.05
Standard deviation	1.06	0.99	0.87	0.94
Mean absolute error	1.90	1.14	0.96	0.73
Maximum error	3.80	3.55	2.06	1.93

performance. However, unlike HF that overestimates the Fe–ring distance, MP2 underestimates it at 147–149 pm [24] (depending on the number of electrons correlated).

Calculations employing the CASSCF and CASPT2 methods perform much better in this respect, giving Fe–ring distances of 171.6 and 161.7 pm, respectively [25]. Subsequently, after correcting the results for basis set superposition errors, an estimated equilibrium value of 164.3 pm was obtained, which is in good agreement with the experimental value of 166 pm. Also CCSD and CCSD(T) calculations predict an equilibrium distance (167.2 and 166.0 pm, respectively [4]) which is in good agreement with the experimental data. Note however, that the coupled-cluster distances were obtained by calculating single-point energies at three Fe–ring distances, and then fitting the potential-energy curve with a second-order polynomial to obtain the equilibrium distance.

The metallocenes studied in this work are manganocene (either doublet or sextet), ferrocene (singlet), cobaltocene (doublet or quartet), nickelocene (singlet or triplet) and ruthenocene (singlet). The geometry data from experimental investigations (taken from Ref. [26]) are given in Table 9. The distance of the metal to the center of the cyclopentadienyl rings differs quite somewhat for the five metal atoms as well as for the multiplet state of the complex. For instance, for manganocene, a difference of more than 32 pm in the distance is observed between the doublet and sextet states.

The geometry of the metallocenes was optimized using all the xc potentials reported in the first part of this paper, employing a few different basis set sizes, ranging from a minimal basis (I) to a TZ2P (VI). The core electrons were either taken explicitly into account (all electrons) or frozen in the calculations; in the latter calculations, the frozen-core electrons comprise the 1*s* electrons of carbon and for the first-row transition metals up to either 3*p* (frozen core 3*p*; for Ru up to 4*p*) or up to the 2*p* level (frozen core 2*p*; for Ru up to 3*d*). For all three types, the optimizations were done in either a nonrelativistic or a scalar relativistic (ZORA) calculation. The mean absolute errors of the computed distances for the eight xc potentials in the four basis sets are given in Tables 10 (nonrelativistic) and 11 (scalar relativistic).

A general improvement of the accuracy is shown by increasing the basis set size, which is most obvious for the all-electron calculations. The mean absolute error, averaged over the eight xc potentials, decreases from 7.70 to 1.77 pm. However, there are some potentials that do not show this pattern; the error of the LDA potential, for instance, decreases in going from basis set I (minimal basis) to II (double-zeta valence), and increases if one uses larger basis sets. The same pattern was reported in the first part of this paper, but there it emerged only after basis set III (double-zeta valence plus polarization) and the error in basis set IV (triple-zeta valence plus polarization) was still smaller than in basis II. Here, the LDA error is larger in basis IV than in basis II, both if one uses the frozen-core or the all-electron calculations.

Table 9. Experimental geometries [25] of metallocenes (pm)

Metal	*r*(C–H)	*r*(C–C)	*r*(metal–ring)
Mn (doublet)	–	141.8	172.0
Mn (sextet)	112.5	142.9	204.1
Fe	110.4	144.0	166.1
Co	109.5	143.0	172.2
Ni	108.3	143.0	182.3
Ru	113.0	143.9	182.3

Table 10. Mean absolute nonrelativistic (*NR*) errors (pm) for first-row metallocenes

Exchange–correlation potential	I	II	IV	VI
Frozen core 3*p*				
Becke–Perdew	7.43	2.77	2.25	–
BLAP3	6.88	5.66	4.99	–
BLYP	7.36	4.52	3.92	–
LDA	8.55	1.23	1.55	–
PBE	7.50	2.52	2.02	–
PW91	7.57	2.53	2.12	–
REVPBE	6.58	3.29	2.61	–
RPBE	7.00	3.53	2.81	–
Average	7.36	3.26	2.78	–
Frozen core 2*p*				
Becke–Perdew	–	1.77	1.39	–
BLAP3	–	4.58	4.05	–
BLYP	–	3.49	2.99	–
LDA	–	2.01	2.46	–
PBE	–	1.60	1.29	–
PW91	–	1.60	1.33	–
REVPBE	–	2.25	1.72	–
RPBE	–	2.49	1.92	–
Average	–	2.47	2.14	–
All electron				
Becke–Perdew	7.68	2.05	1.39	1.00
BLAP3	7.21	4.92	4.08	3.18
BLYP	7.69	3.78	3.05	2.17
LDA	8.81	1.87	2.47	3.05
PBE	7.83	1.82	1.28	1.11
PW91	7.82	1.79	1.34	1.13
REVPBE	7.30	2.53	1.72	1.18
RPBE	7.23	2.78	1.93	1.30
Average	7.70	2.69	2.16	1.77

The difference between the frozen-core 3*p*, frozen-core 2*p* and all-electron results is not negligible. For the minimal basis (I), the frozen-core 3*p* gives a better performance than the all-electron calculations; for the larger basis sets, the situation is reversed. In basis II, the best performance is observed with the frozen-core 2*p* option, which gives a mean absolute error that is 0.2–0.3 pm smaller than that for the all-electron case. In basis set IV, these two options perform equally well, and considerably better (0.8–0.9 pm) than the frozen core 3*p* option.

The "best" xc potentials are for the larger basis sets and the all-electron/frozen-core 2*p* options, Becke–Perdew, PBE and PW91, as was reported in the first part of this paper. For the frozen-core 3*p* option in the larger basis sets, the LDA performs best; in basis II, the mean

Table 11. Mean absolute scalar relativistic (*SR*) errors using the zeroth-order regular approximation approach errors (pm) for first-row metallocenes

Exchange–correlation potential	I	II	IV	VI
Frozen core 3*p*				
Becke–Perdew	–	2.47	2.01	–
BLAP3	–	5.31	4.71	–
BLYP	–	4.20	3.66	–
LDA	–	1.38	1.77	–
PBE	–	2.22	1.78	–
PW91	–	2.26	1.88	–
REVPBE	–	2.97	2.35	–
RPBE	–	3.22	2.56	–
Average	–	3.00	2.59	–
Frozen core 2*p*				
Becke–Perdew	–	1.54	1.18	–
BLAP3	–	4.21	3.66	–
BLYP	–	3.14	2.63	–
LDA	–	2.31	2.76	–
PBE	–	1.40	1.07	–
PW91	–	1.41	1.11	–
REVPBE	–	1.93	1.44	–
RPBE	–	2.12	1.59	–
Average	–	2.26	1.93	–
All electron				
Becke–Perdew	7.83	1.72	1.19	1.22
BLAP3	7.37	4.53	3.69	2.74
BLYP	7.85	3.43	2.67	1.76
LDA	8.97	2.18	2.80	3.42
PBE	7.92	1.58	1.06	1.38
PW91	7.97	1.59	1.15	1.39
REVPBE	7.40	2.17	1.45	1.08
RPBE	7.33	2.39	1.59	1.12
Average	7.83	2.45	1.95	1.76

absolute error is only 1.23 pm, a value not reached by any other potential in any basis set with the frozen-core 3*p* option. However, using the frozen-core 2*p* or the all-electron option, this value is reached in the larger basis sets (IV, VI) by other xc potentials. In the minimal basis, the BLAP3 and REVPBE give generally the "best" performance, but as the mean absolute error is about 4 times as large as the value in the larger basis sets, it is of limited value.

The influence of the scalar relativistic corrections is, apart from the all-electron calculations in basis VI, small (0.2 pm) but improving. This effect is of the same order of magnitude as the effect observed due to a slight mismatch between the energy expression and the potential in the ZORA approach, which leads to an optimized geometry with zero gradient that may differ from the point of lowest energy by some 0.1 pm. Therefore, the effect of the relativistic corrections can safely be ignored.

The all-electron results in basis VI show different patterns for different xc potentials. For some, like Becke–Perdew, PBE and PW91, the mean absolute error increases relative to the nonrelativistic results, while for others, like LDA, the error decreases. Still, these changes are of the same small magnitude (0.2 pm) and therefore are not significant.

For the first-row transition metals, the effect of the inclusion of relativistic corrections is small, but for ruthenocene, it probably can no longer be safely ignored. As the relativistic corrections will have an effect mainly on the Ru–ring distance and not as much on the C–C or C–H distance, only the Ru–ring distance is taken into account for the mean absolute error. The errors for the xc potentials in several basis sets and with different options for the core electrons are given in Table 12. As expected, the relativistic corrections now do have a significant effect on the values of the mean absolute error, which are improved by an amount of 1.4–2.2 pm. The same trends are observed as before, for example, generally speaking the error decreases with increasing basis set size (apart from the LDA potential), the frozen-core 2*p* option performs better than the frozen-core 3*p* option (except for the LDA potential), and BLAP3 and BLYP perform significantly worse than the other potentials.

The multiplet states of cobaltocene, nickelocene and manganocene lead in all cases to the same ground state, respectively a doublet, a triplet and a doublet. The other states are less favored by 21 kcal/mol (quartet cobaltocene), 14 kcal/mol (singlet nickelocene) and 14 kcal/mol (sextet manganocene) with the Becke–Perdew xc potential in basis set IV using the all-electron option. These values differ by a few kilocalories per mole with different basis sets and/or xc potentials, but the relative ordering of the multiplet states does not.

The relative ordering of the conformations of the metallocenes is also rather constant over the range of xc

Table 12. Mean absolute SR/NR errors (pm) for the Ru–ring distance

Exchange–correlation potential	II/NR	IV/NR	II/SR	IV/SR	V/SR
Frozen core 3*p*					
Becke–Perdew	9.01	6.69	6.84	4.54	–
BLAP3	15.64	13.43	13.02	10.89	–
BLYP	13.44	11.36	10.90	8.91	–
LDA	3.52	1.60	1.68	0.41	–
PBE	8.18	5.75	6.13	3.63	–
PW91	8.61	6.12	6.18	3.92	–
REVPBE	9.30	6.79	7.20	4.68	–
RPBE	9.72	7.17	7.63	5.04	–
Average	9.68	7.36	7.45	5.25	–
Frozen core 2*p*					
Becke–Perdew	5.59	3.57	3.99	1.82	–
BLAP3	11.90	9.91	9.89	7.77	–
BLYP	9.84	8.07	7.91	5.99	–
LDA	0.39	1.28	1.02	2.96	–
PBE	4.82	2.73	3.36	0.99	–
PW91	5.12	3.21	3.54	1.32	–
REVPBE	5.87	3.62	4.29	1.91	–
RPBE	6.25	3.97	4.65	2.25	–
Average	6.22	4.55	4.83	3.13	–
All electron					
Becke–Perdew	–	–	4.82	2.47	1.18
BLAP3	–	–	10.83	8.64	7.42
BLYP	–	–	8.81	6.77	5.52
LDA	–	–	0.27	2.49	3.83
PBE	–	–	4.16	1.64	0.33
PW91	–	–	4.22	2.10	0.60
REVPBE	–	–	5.17	2.62	1.29
RPBE	–	–	5.56	2.99	1.65
Average	–	–	5.48	3.72	2.73

potentials and basis sets; in nearly all cases the eclipsed conformation is favored. The energy difference between the two conformations, however, differs between the different metallocenes, 0.4 kcal/mol (doublet cobaltocene), 0.1 kcal/mol (quartet cobaltocene), 1.0 kcal/mol (ferrocene), 1.2 kcal/mol (doublet manganocene), 0.01 kcal/mol (sextet manganocene), 0.1 kcal/mol (singlet or triplet nickelocene) and 0.5 kcal/mol (ruthenocene), using the Becke–Perdew xc potential in basis set IV. For quartet cobaltocene, sextet manganocene and nickelocene, the energy difference is too small to be considered significant, and both conformations are equally favorable. Again, these values change somewhat by using another xc potential and/or basis set, but the relative ordering of the conformations remains roughly intact.

Conclusions

The geometries of a set of small molecules were optimized using eight different xc potentials in a few different basis sets of Slater-type orbitals, ranging from a minimal basis (I) to a TZ2P (VI). This enables a comparison of the accuracy of the xc potentials in a certain basis set, which can be related to the accuracies of wavefunction-based methods such as HF and coupled cluster. Four different checks were done on the accuracy by looking at the mean error, standard deviation, mean absolute error and maximum error. It was shown that the mean absolute error decreases with increasing basis set size, and reaches a basis set limit at basis VI. With this basis set, the mean absolute errors of the xc potentials are of the order of 0.7–1.3 pm. This is comparable to the accuracy obtained with CCSD and MP2/MP3 methods, but is still larger than the accuracy that can be obtained with the CCSD(T) method (0.1–0.2 pm). For the smaller all-electron basis sets the LDA is found to perform well; generally speaking the best-performing xc potentials are found to be Becke–Perdew, PBE and PW91, which perform as well as the hybrid B3LYP potential.

In the second part of this paper, we reported the optimization of the geometry of five metallocenes with the same potentials and basis sets, either in a nonrelativistic or in a scalar relativistic calculation using the ZORA approach. For the first-row transition-metal complexes, the relativistic corrections have a negligible effect on the optimized structures, but for ruthenocene they improve the optimized Ru–ring distance by some 1.4–2.2 pm. In the largest basis set used, the absolute mean error is again of the order of 1.0 pm. As the wavefunction-based methods give a poor performance for metallocenes (HF, MP2) or the size of the system makes treatment with accurate methods such as CCSD(T) in a reasonable basis set cumbersome, the good performance of DFT calculations for these molecules is very promising; even more so as DFT is an efficient method that can be used without problems on systems of this size, or larger.

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