

Calibration of Modern Density Functional Theory Methods for the Prediction of ^{57}Fe Mössbauer Isomer Shifts: Meta-GGA and Double-Hybrid Functionals

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Five density functionals including GGA (generalized gradient approximation) (BP86), meta-GGA (TPSS), hybrid meta-GGA (TPSSH), hybrid (B3LYP), and double-hybrid functionals (B2PLYP) were calibrated for the prediction of ^{57}Fe Mössbauer isomer shifts on a set of 20 iron-containing molecules. The influence of scalar relativistic effects and the basis set dependence of the predictions were investigated.

Mössbauer (MB) spectroscopy has become one of the most important analytical tools in the field of (bio)inorganic iron chemistry. This is due to the high importance of iron for all forms of life¹ and the rapidly increasing popularity of iron in catalysis.² In combination with rapid freeze quenching, MB spectroscopy provides a very powerful spectroscopic approach to the analysis of short-lived intermediates.^{3,4} The two primary parameters that can be obtained from a MB spectrum of a given iron center are the isomer shift (IS) and the quadrupole splitting.⁵ As shown by decades of experience, these two parameters are closely related to the electron-density distribution. In particular, the IS is known to be directly proportional to the total electron density at the iron nucleus.

During the past 6 years, it has become evident that density functional theory provides a reliable tool for the prediction

and interpretation of MB ISs.^{6–8} An elegant linear response theory for this property has recently been proposed by Filatov.⁷ Various workers have established an excellent linearity between nonrelativistic and also relativistic electron densities at the iron nucleus and the observed ISs.^{6d–f,7,8} These calibration curves have shown a remarkable robustness in the sense that no significant dependence of the calibration constants on the oxidation state, spin state, or coordination number of the iron has been detected. However, owing to basis set incompleteness errors and shortcomings of present day density functionals, the correlation has to be established for each combination of functional and basis set. Previously, it was speculated that this requires special basis sets with added flexibility in the core region.⁸ Later studies have speculated that this might not be the case and that standard basis sets that typically only include a single basis function for each core orbital already provide adequate accuracy.^{16d,f} The present work therefore has the triple purpose of (a) recalibrating the two most widely used GGA (BP86⁹) and hybrid (B3LYP¹⁰) functionals for use with the standard triple- ζ basis set of Ahlrichs and co-workers (TZVP),¹¹ (b) extending the calibration to the case of scalar relativistic corrections provided by the ZORA¹² method using recently

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Table 1. Linear Fit Data for ^{57}Fe MB IS Predictions Using the Linear Equation $\delta = \alpha(\rho - C) + \beta$

functional	basis	α	β	C	R^2	std dev (mm/s)
BP86	CP(PPP)	-0.425	7.916	11 810	0.95	0.11
	TZVP	-0.340	1.034	11 580	0.93	0.12
	TZVP ^a	-0.362	4.957	13 800	0.92	0.12
B3LYP	CP(PPP)	-0.366	2.852	11 810	0.98	0.09
	TZVP	-0.298	1.118	11 580	0.94	0.11
	TZVP ^a	-0.307	4.045	13 770	0.97	0.08
TPSS	CP(PPP)	-0.421	5.154	11 810	0.96	0.10
	TZVP	-0.336	1.327	11 580	0.90	0.14
	TZVP ^a	-0.365	1.385	13 800	0.94	0.10
TPSSh	CP(PPP)	-0.376	4.130	11 810	0.97	0.08
	TZVP	-0.321	1.466	11 580	0.96	0.10
	TZVP ^a	-0.322	1.830	13 780	0.97	0.08
B2PLYP	CP(PPP)	-0.336	2.642	11 810	0.97	0.09
	TZVP	-0.261	1.483	11 580	0.84	0.12
	TZVP ^a	-0.311	2.256	13 790	0.97	0.08

^a ZORA recontracted basis sets.

reported recontracted all-electron relativistic basis sets¹³ and, most importantly, (c) calibrating the newly emerging classes of meta-GGA (TPSS¹⁴), hybrid meta-GGA (TPSSh¹⁵), and perturbatively corrected double-hybrid (DHDF) functionals (B2PLYP^{16a}) for use in MB spectroscopy. The theory of first-order properties in the framework of DHDFs has recently been developed and successfully applied.^{16c,e} Presently, these functionals offer unprecedented accuracy in the calculation of thermodynamic,^{16a,b,f} kinetic,^{16a,b,f} and structural^{16c} parameters as well as excitation energies.^{16d}

Table 1 shows a comparison of the R^2 values, which are measures for the quality of a given linear fit, and the actual fit data for the different levels of theory and sizes of basis sets.¹⁷ Consistent with previous results,²⁰ the hybrid density

functionals B3LYP and TPSSh yield linear fits of superior quality compared to the pure density functionals BP86 and TPSS. Similarly, excellent results are obtained with the DHDF B2PLYP. Note, however, that with the relatively small TZVP basis set for the iron atom, the linear fit obtained by the B2PLYP functional, is of rather low quality. This finding is probably due to the strong intrinsic basis set dependence of the perturbative second-order contributions to the correlation part. A common result for all five density functionals is the substantial improvement of the linear fits when the enlarged CP(PPP) basis set⁸ for the iron atom is used. Hence, the limited additional computational effort for the larger basis set is justified. We have carefully verified that further enlargement of the basis set by additional polarization functions neither changes the fit parameters nor leads to improved results. Calculations using the ZORA Hamiltonian and recontracted all-electron relativistic basis sets provide clear improvements over the nonrelativistic TZVP results. However, after careful study of this subject, it was found that these improvements can be traced back to the increased flexibility of the recontracted basis sets in the semicore and valence regions rather than to the scalar relativistic corrections themselves (cf. the Supporting Information).²² As pointed out earlier, this is rationalized by the finding that the contributions of the 1s and 2s core orbitals to the electron densities at the iron nucleus are to a very good approximation constant throughout iron chemistry.^{8a,b}

To the best of our knowledge, the current work provides the most complete list of calibration constants for a larger range of modern functionals and basis sets, although similar standard deviations have been reported previously.^{6d-f,7,8} Taken together, the present work enables researchers to obtain excellent predictions for MB ISs. An even wider use of this stable, reliable, and efficient method to many problems in iron chemistry is anticipated.

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Supporting Information Available: Cartesian coordinates of all investigated molecules, results for BP86-optimized structures, further enlarged basis sets, and ZORA recontracted basis sets, and the leave-one-out analyses for the quality of the linear fits. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (17) In this work, the five functionals mentioned in the text were calibrated on a training set of 20 benchmark iron complexes described earlier.⁸ The training set includes small molecules as well as larger coordination compounds such as iron porphyrins. All calculations were carried out with the ORCA package.¹⁸ Geometries were optimized at the TPSS/TZVP and BP86/TZVP level. Wherever possible, crystallographically determined structures were used as starting points. The TPSS functional has been shown to obtain excellent geometries.²¹ Table 1 shows the results for geometries optimized with the TPSS functional. The equivalent of Table 1 for BP86-optimized geometries is given in the Supporting Information. The COSMO model¹⁹ has been chosen to simulate an aqueous solution environment in all cases. Open-shell molecules were described with unrestricted Kohn–Sham determinants. Accurate numerical integration was ensured.^{8a}
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(22) It is well-known that scalar relativistic calculations with point-like nuclei lead to divergent behavior of the s orbitals close to the nucleus. Actual divergence is prevented by the contraction of the Gaussian sets for the innermost s function.²¹ However, the crucial changes of the orbital shapes in the valence region are still accurately represented by such calculations.