

Supplementary Materials

Prediction of ^{57}Fe Mössbauer Nuclear Quadrupole Splittings with Hybrid and Double-Hybrid Density Functionals

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Table S1: Theoretical V_c (in a.u.) of the Cu nucleus in CuF ($r_e = 1.7449$ Å). The experimental values is -0.425 a.u.

<i>Ab initio</i>	V_c	Error	Hybrid functional	V_c	Error	Double-hybrid functional	V_c	Error		
HF	-1.252	-0.827	BH&HLYP	-0.391	0.034	ω B97X-2	0.023	0.448		
CCSD	-0.553	-0.128	B3LYP	0.350	0.775	PWPB95	0.010	0.435		
CCSD(T)	-0.449	-0.024	CAM-B3LYP	0.167	0.592	B2PLYP model	B2PLYP	0.104	0.529	
CCSD(T) ^{a)}	-0.433	-0.008	PW6B95	0.101	0.526	m PW2PLYP	0.002	0.427		
			M06-2X	-0.313	0.112	B2GP-PLYP	-0.110	0.315		
CASSCF(9 <i>o</i>)	1.704	2.129	ω B97XD	0.184	0.609	B2K-PLYP	-0.231	0.194		
MRCI(9 <i>o</i>)	1.827	2.252	PBE <i>n</i>	PBE0	0.135	0.560	B2T-PLYP	-0.042	0.383	
MRAQCC(9 <i>o</i>)	1.724	2.149		PBE38	-0.191	0.234	DSD model	DSD-BLYP	-0.206	0.219
				PBE50	-0.489	-0.064		DSD-PBEP86	-0.176	0.249
CASSCF(14 <i>o</i>)	-0.962	-0.537	TPSS <i>n</i>	TPSSh	0.395	0.820		DSD-PBEB95	-0.171	0.254
MRCI(14 <i>o</i>) ^{b)}	-0.603	-0.178		TPSS0	0.016	0.441	DH/QIDH model	PBE-0DH	-0.213	0.212
MRAQCC(14 <i>o</i>) ^{b)}	-0.367	0.058		TPSS38	-0.288	0.137		PBE-QIDH	-0.358	0.067
				TPSS50	-0.568	-0.143		RSX-0DH	-0.463	-0.038
			SCAN <i>n</i>	SCAN0	-0.034	0.391		RSX-QIDH	-0.485	-0.060
				SCAN38	-0.383	0.042	LR corrected model	ω B2PLYP	-0.167	0.258
				SCAN50	-0.623	-0.198		ω B2GP-PLYP	-0.274	0.151
			r SCAN <i>n</i>	r SCAN0	-0.094	0.331		ω B88PP86	-0.163	0.262
				r SCAN38	-0.351	0.074		ω PBEP86	-0.229	0.196
				r SCAN50	-0.589	-0.164	DSD/DOD-2019 model	DOD-SCAN-D3(BJ)	-0.180	0.245
			r^2 SCAN <i>n</i>	r^2 SCAN0	-0.116	0.309		noDispSD-SCAN69	-0.149	0.276
				r^2 SCAN38	-0.370	0.055		revDSD-PBEP86-D3(BJ)	-0.126	0.299
				r^2 SCAN50	-0.602	-0.177		revDSD-BLYP-D3(BJ)	-0.160	0.265
								revDOD-PBEP86-D3(BJ)	-0.137	0.288
						r^2 SCAN-2023 model	r^2 SCAN-0DH	-0.363	0.062	
							r^2 SCAN-CIDH	-0.398	0.027	
							r^2 SCAN-QIDH	-0.469	-0.044	
							r^2 SCAN0-2	-0.488	-0.063	
							Pr^2 SCAN50	-0.116	0.309	
							Pr^2 SCAN69	-0.313	0.112	

^{a)} All the core electrons are correlated.

^{b)} Configurations with *weight* $\geq 0.01\%$ are selected.

Table S2: Natural configuration of the Cu atom in CuF.

Method	Natural electron configuration
HF	$3d^{9.92}4s^{0.14}4p^{0.03}$
CCSD	$3d^{9.73}4s^{0.28}4p^{0.06}4d^{0.08}$
CCSD(T)	$3d^{9.70}4s^{0.30}4p^{0.07}4d^{0.09}$
CASSCF(9o)	$3d^{9.20}4s^{0.90}4p^{0.03}4d^{0.01}$
MRCI(9o)	$3d^{9.19}4s^{0.87}4p^{0.05}4d^{0.05}$
MRAQCC(9o)	$3d^{9.17}4s^{0.86}4p^{0.08}4d^{0.06}$
CASSCF(14o)	$3d^{9.80}4s^{0.23}4p^{0.03}4d^{0.07}$
MRCI(14o)	$3d^{9.75}4s^{0.25}4p^{0.05}4d^{0.08}$
MRAQCC(14o)	$3d^{9.71}4s^{0.28}4p^{0.06}4d^{0.08}$
BH&HLYP	$3d^{9.87}4s^{0.26}4p^{0.03}$
B3LYP	$3d^{9.81}4s^{0.39}4p^{0.04}$
B2PLYP (SCF part)	$3d^{9.87}4s^{0.26}4p^{0.03}$
B2PLYP	$3d^{9.72}4s^{0.38}4p^{0.05}4d^{0.06}$
r2SCAN-CIDH (SCF part)	$3d^{9.88}4s^{0.23}4p^{0.03}$
r2SCAN-CIDH	$3d^{9.81}4s^{0.30}4p^{0.04}4d^{0.03}$

Table S3: ΔE_Q results (in mm/s) of ^{57}Fe by selected hybrid functionals. ^{a)}

Mol. ^{b)}	N_{atom}^{2S+1}	η ^{c)}	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	Expt.
1*	42 ²	0.50	-0.33	0.37	-0.32	-0.24	-0.35	-0.25	-0.50	-1.16	-0.30	-1.17	-0.30	-0.40
2*	38 ¹	0.79	-0.47	-0.50	-0.43	-0.38	-0.47	-0.39	-0.47	-0.38	-0.46	-0.39	-0.47	0.29
3*	44 ¹	0.79	-0.73	0.74	0.74	0.73	-0.75	0.72	-0.72	0.72	-0.73	0.72	-0.74	0.69
4	18 ⁴	0.45	3.17	2.90	3.00	2.80	3.11	2.75	3.02	2.60	2.93	2.59	2.91	2.10
5	50 ¹	0.45	-0.90	-0.95	-0.94	-0.91	-0.90	-0.91	-0.90	-0.92	-0.92	-0.92	-0.91	-0.74
		0.44	-0.90	-0.94	-0.94	-0.91	-0.90	-0.89	-0.89	-0.91	-0.91	-0.91	-0.91	
6	59 ¹	0.34	-1.14	-1.12	-1.19	-1.19	-1.14	-1.17	-1.12	-1.20	-1.15	-1.20	-1.15	-1.14
7	17 ⁵	0.06	-4.11	-4.01	-4.08	-4.05	-4.09	3.70	3.78	-4.05	-4.09	3.87	-4.09	-3.97
8	33 ⁶	0.02	-0.34	-0.35	-0.33	-0.35	-0.32	-0.35	-0.33	-0.35	-0.33	-0.35	-0.32	-0.62
9	29 ²	0.26	-0.77	-0.90	-0.78	-0.71	-0.80	-0.76	-0.83	-0.78	-0.84	-0.78	-0.84	-0.69
10*	49 ⁵	0.81	-3.65	-3.58	-3.57	-3.51	-3.59	3.31	3.40	-3.48	-3.56	-3.48	-3.55	-3.24
11	43 ⁵	0.11	3.85	3.85	3.79	3.73	3.79	3.58	3.65	3.73	3.79	3.72	3.78	3.62
12	43 ⁵	0.12	3.92	3.85	3.85	3.79	3.86	3.64	3.72	3.80	3.85	3.78	3.84	3.61
13	17 ¹	0.12	-1.59	-1.55	-1.59	-1.54	-1.57	-1.53	-1.57	-1.56	-1.59	-1.56	-1.59	-1.34
14	45 ²	0.18	-2.04	-2.29	-2.01	-1.92	-1.86	-1.66	-1.65	-1.87	-1.82	-1.85	-1.79	-2.24
15	39 ⁶	0.63	2.59	2.34	2.52	2.25	2.60	2.16	2.51	2.14	2.54	2.13	2.53	0.62
16*	42 ¹	0.76	-1.56	-1.54	-1.59	-1.58	-1.51	-1.52	-1.48	-1.58	-1.53	-1.58	-1.52	-1.63
17	49 ¹	0.23	0.33	0.37	0.35	0.35	0.34	0.33	0.33	0.34	0.34	0.34	0.34	0.43
18*	54 ¹	0.90	-0.59	-0.64	-0.59	-0.53	-0.59	-0.55	-0.59	-0.54	-0.59	-0.54	-0.59	0.48
19	71 ¹	0.64	0.49	0.45	0.51	0.52	0.47	0.53	0.48	-0.55	0.49	-0.54	0.49	-0.83
20*	54 ¹	0.62	0.57	0.65	0.55	0.49	0.57	0.53	0.59	0.49	0.57	0.50	0.57	-0.35
21	44 ¹	0.38	0.97	1.03	0.97	0.92	0.96	0.94	0.97	0.94	0.97	0.94	0.97	0.73
22	27 ¹	0.58	1.13	1.20	1.13	1.09	1.12	1.09	1.11	1.10	1.13	1.10	1.13	0.89
23*	44 ⁵	0.98	-1.86	-1.85	-1.87	-1.82	-1.87	1.83	1.87	-1.84	-1.87	-1.84	-1.87	-1.42
24	58 ³	0.48	-1.41	-1.27	-1.40	-1.10	-1.38	-1.21	-1.39	-1.19	-1.43	-1.20	-1.43	-1.24
25	25 ⁴	0.49	-2.67	-2.68	-2.65	-2.66	-2.62	-2.58	-2.56	-2.67	-2.64	-2.68	-2.64	-2.05
26	21 ¹	0.00	4.14	4.14	4.01	3.62	4.01	3.80	4.09	3.65	4.03	3.65	4.03	2.41
27	13 ⁶	0.42	-0.87	-0.82	-0.85	-0.90	-0.85	-0.87	-0.83	-0.87	-0.83	-0.87	-0.83	-1.23
28	22 ²	0.49	-1.29	-1.42	-1.29	-1.22	-1.30	-1.28	-1.35	-1.29	-1.35	-1.29	-1.35	-1.12
29	51 ²	0.11	0.77	0.59	0.79	0.68	0.74	0.70	0.73	0.81	0.89	0.81	0.89	0.89
30	21 ⁵	0.13	1.96	1.96	1.89	1.84	1.90	1.67	1.76	1.79	1.87	1.77	1.86	1.80
31	56 ⁵	0.34	2.63	2.64	2.56	2.50	2.57	2.34	2.44	2.46	2.55	2.45	2.54	2.10
32	25 ⁵	0.73	2.75	2.74	2.68	2.63	2.69	2.48	2.56	2.60	2.67	2.59	2.66	2.36
MaxE ^{d)}			1.73	1.73	1.60	1.35	1.60	7.67	7.75	1.24	1.62	7.84	1.62	
MAE ^{d)}			0.33	0.33	0.31	0.27	0.32	0.50	0.54	0.25	0.32	0.49	0.32	
MAE ^{e)}			0.30	0.30	0.28	0.24	0.29	0.24	0.28	0.25	0.28	0.25	0.28	

^{a)} The hybrid functionals are BH&HLYP (**H-1**), M06-2X (**H-2**), PBE50 (**H-3**), TPSS38 (**H-4**), TPSS50 (**H-5**), SCAN38 (**H-6**), SCAN50 (**H-7**), r SCAN38 (**H-8**), r SCAN50 (**H-9**), r^2 SCAN38 (**H-10**), and r^2 SCAN50 (**H-11**).

^{b)} The molecule with an asterisk means that the sign of ΔE_Q is theoretically uncertain and therefore $|\Delta E_Q|$ is used for error analysis.

- ^{c)} Calculated by r^2 SCAN-CIDH.
- ^{d)} Maximum error and mean absolute error. Molecule **15** has been excluded.
- ^{e)} Mean absolute error of $|\Delta E_Q|$. Molecule **15** has been excluded.

Table S4: ΔE_Q results (in mm/s) of ^{57}Fe by selected double-hybrid functionals. ^{a)}

Mol. ^{b)}	N_{atom}^{2S+1}	Density ^{c)}	η ^{d)}	DH-1	DH-2	DH-3	DH-4	DH-5	DH-6	DH-7	DH-8	DH-9	DH-10	DH-11	DH-12	Expt.
1*	42^2	HFun		-0.33	0.34	-0.32	-0.53	-0.53	-0.52	-0.50	-0.49	-0.47	-0.48	-0.32	-0.43	
		UnRlx		-0.31	0.33	-0.30	-0.49	-0.49	-0.49	-0.47	-0.45	-0.43	-0.44	-0.29	-0.42	
		Rlx	0.50	-0.44	-1.01	0.33	0.23	-0.74	0.23	-0.72	-0.89	-0.80	-1.13	-0.32	0.24	-0.40
2*	38^1	HFun		-0.52	-0.68	-0.48	-0.65	-0.67	-0.65	-0.64	-0.62	-0.60	-0.64	-0.44	-0.56	
		UnRlx		-0.48	-0.63	-0.45	-0.59	-0.60	-0.60	-0.60	-0.56	-0.54	-0.57	-0.41	-0.54	
		Rlx	0.79	-0.29	-0.33	-0.29	0.20	0.19	-0.27	-0.31	0.18	0.21	0.18	0.21	-0.40	0.29
3*	44^1	HFun		-0.73	-0.73	-0.73	-0.73	-0.73	-0.75	-0.76	-0.75	-0.74	-0.73	0.74	-0.78	
		UnRlx		-0.73	-0.73	-0.73	-0.73	-0.73	-0.75	-0.75	-0.75	-0.73	-0.73	0.73	-0.78	
		Rlx	0.79	0.74	0.77	0.73	0.78	0.79	0.79	0.80	0.82	0.78	0.79	0.74	0.79	0.69
4	18^4	HFun		2.97	3.45	2.87	3.48	3.51	3.49	3.45	3.37	3.34	3.35	2.99	3.33	
		UnRlx		2.99	3.49	2.88	3.51	3.55	3.52	3.47	3.41	3.36	3.38	2.99	3.34	
		Rlx	0.45	3.28	3.70	3.10	3.16	3.10	3.24	3.25	3.07	3.07	3.20	2.69	3.20	2.10
5	50^1	HFun		-0.89	0.81	-0.90	0.81	0.80	0.84	0.85	0.85	0.86	0.83	-0.94	-0.92	
				-0.88	0.80	-0.89	0.81	0.80	0.83	0.85	0.85	0.85	0.82	-0.93	-0.91	
		UnRlx		-0.91	0.83	-0.91	-0.85	-0.84	-0.86	-0.88	-0.89	-0.89	-0.87	-0.95	-0.93	
				-0.90	0.83	-0.91	-0.84	-0.83	-0.86	-0.87	-0.88	-0.88	-0.86	-0.94	-0.92	
		Rlx	0.45	-0.98	-1.07	-0.95	-1.17	-1.23	-1.09	-1.07	-1.23	-1.13	-1.21	-0.98	-0.96	-0.74
6	59^1		0.44	-0.97	-1.07	-0.95	-1.16	-1.22	-1.08	-1.06	-1.22	-1.12	-1.20	-0.98	-0.96	
		HFun		-1.11	-0.94	-1.14	-0.98	-0.96	-1.02	-1.03	-1.03	-1.04	-1.00	-1.18	-1.15	
		UnRlx		-1.13	-0.99	-1.16	-1.03	-1.02	-1.06	-1.07	-1.09	-1.08	-1.06	-1.20	-1.17	
7	17^5	Rlx	0.34	-1.36	-1.47	-1.32	-1.67	-1.76	-1.56	-1.51	-1.78	-1.61	-1.74	-1.39	-1.32	-1.14
		HFun		-4.10	-4.10	-4.09	-4.11	-4.11	-4.12	-4.11	-4.10	-4.10	-4.09	-4.08	-4.11	
		UnRlx		-4.12	-4.16	-4.10	-4.17	-4.19	-4.18	-4.15	-4.17	-4.15	-4.16	-4.10	-4.13	
8	33^6	Rlx	0.06	-4.06	-4.10	-4.05	-4.12	-4.14	-4.13	-4.12	-4.12	-4.10	-4.10	-4.04	-4.11	-3.97
		HFun		-0.31	-0.26	-0.32	-0.28	-0.27	-0.29	-0.28	-0.28	-0.28	-0.27	-0.33	-0.32	
		UnRlx		-0.31	-0.26	-0.32	-0.29	-0.28	-0.30	-0.28	-0.29	-0.29	-0.28	-0.34	-0.32	
9	29^2	Rlx	0.02	-0.35	-0.34	-0.36	-0.39	-0.39	-0.38	-0.36	-0.40	-0.37	-0.39	-0.39	-0.35	-0.62
		HFun		-0.89	-1.00	-0.86	-0.94	-0.96	-0.91	-0.93	-0.92	-0.92	-0.95	-0.79	-0.83	
		UnRlx		-0.88	-0.99	-0.85	-0.93	-0.95	-0.90	-0.93	-0.91	-0.92	-0.94	-0.79	-0.83	
10*	49^5	Rlx	0.26	-0.76	-0.82	-0.75	-0.71	-0.70	-0.71	-0.77	-0.67	-0.73	-0.70	-0.67	-0.75	-0.69
		HFun		-3.59	-3.67	-3.56	-3.72	-3.72	-3.72	-3.67	-3.66	-3.66	-3.67	-3.57	-3.65	
		UnRlx		-3.60	-3.72	-3.57	-3.77	-3.78	-3.76	-3.71	-3.72	-3.70	-3.73	-3.59	-3.66	
11	43^5	Rlx	0.81	-3.50	-3.59	-3.48	-3.59	-3.59	-3.61	-3.59	-3.53	-3.55	-3.54	-3.47	-3.60	-3.24
		HFun		3.80	3.85	3.78	3.89	3.89	3.90	3.85	3.85	3.84	3.86	3.79	3.84	
		UnRlx		3.81	3.91	3.79	3.94	3.96	3.95	3.90	3.91	3.88	3.91	3.81	3.86	
12	43^5	Rlx	0.11	3.73	3.79	3.72	3.83	3.84	3.85	3.81	3.78	3.78	3.78	3.71	3.81	3.62
		HFun		3.86	3.91	3.84	3.94	3.94	3.97	3.92	3.92	3.90	3.92	3.86	3.91	
		UnRlx		3.88	3.96	3.86	3.99	4.00	4.01	3.96	3.98	3.95	3.97	3.87	3.93	
13	17^1	Rlx	0.12	3.79	3.85	3.78	3.89	3.91	3.92	3.89	3.86	3.84	3.85	3.77	3.88	3.61
		HFun		-1.59	-1.53	-1.58	-1.55	-1.54	-1.61	-1.61	-1.59	-1.57	-1.55	-1.59	-1.69	

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Table S4: *Continued from previous page.*

Mol. ^{b)}	N_{atom}^{2S+1}	Density ^{c)}	η ^{d)}	DH-1	DH-2	DH-3	DH-4	DH-5	DH-6	DH-7	DH-8	DH-9	DH-10	DH-11	DH-12	Expt.
14	45 ²	UnRlx		-1.57	-1.51	-1.56	-1.52	-1.51	-1.60	-1.60	-1.57	-1.55	-1.52	-1.56	-1.68	
		Rlx	0.12	-1.68	-2.29	-1.63	-2.43	-2.70	-2.18	-2.09	-2.40	-2.12	-2.46	-1.64	-1.75	-1.34
		HFun		-1.73	-1.69	-1.78	-1.84	-1.81	-1.94	-1.88	-1.86	-1.84	-1.82	-2.00	-2.06	
15	39 ⁶	UnRlx		-1.75	-1.72	-1.79	-1.88	-1.85	-1.97	-1.90	-1.90	-1.87	-1.85	-2.01	-2.07	
		Rlx	0.18	-2.03	-4.21	-1.99	-2.43	-2.53	-2.43	-2.34	-2.62	-2.37	-2.52	-2.19	-2.24	-2.24
		HFun		2.63	2.81	2.52	2.94	2.85	2.93	2.80	2.89	2.86	2.89	2.51	2.79	
16*	42 ¹	UnRlx		2.64	2.86	2.52	2.98	2.90	2.97	2.83	2.94	2.89	2.94	2.52	2.80	
		Rlx	0.63	2.33	2.75	2.25	2.43	2.67	2.52	2.66	2.34	2.39	2.33	2.06	2.59	0.62
		HFun		-1.45	-1.19	-1.50	-1.27	-1.24	-1.33	-1.30	-1.31	-1.36	-1.29	-1.58	-1.50	
17	49 ¹	UnRlx		-1.51	-1.28	-1.54	-1.38	-1.37	-1.41	-1.38	-1.42	-1.45	-1.41	-1.63	-1.53	
		Rlx	0.76	2.05	2.62	1.93	2.99	3.25	2.58	2.38	3.05	2.71	3.13	2.06	1.85	-1.63
		HFun		0.33	0.31	0.33	0.31	0.31	0.32	0.33	0.33	0.32	0.32	0.34	0.35	
18*	54 ¹	UnRlx		0.33	0.32	0.34	0.32	0.32	0.33	0.33	0.34	0.33	0.32	0.35	0.35	
		Rlx	0.23	0.36	0.37	0.36	0.39	0.41	0.39	0.39	0.43	0.40	0.41	0.38	0.38	0.43
		HFun		-0.63	-0.77	-0.60	-0.74	-0.76	-0.74	-0.74	-0.73	-0.71	-0.74	-0.59	-0.68	
19	71 ¹	UnRlx		-0.60	-0.72	-0.57	-0.67	-0.68	-0.69	-0.70	-0.66	-0.65	-0.67	-0.56	-0.66	
		Rlx	0.90	-0.50	-0.52	-0.50	0.56	0.59	0.54	-0.53	0.61	0.54	0.58	0.50	-0.56	0.48
		HFun		0.45	0.38	0.47	0.39	0.39	0.41	0.41	0.42	0.42	0.40	0.50	0.47	
20*	54 ¹	UnRlx		0.47	0.37	0.48	0.39	0.38	0.41	0.41	0.43	0.42	0.40	0.52	0.48	
		Rlx	0.64	-0.69	-0.70	-0.67	-0.92	-0.99	-0.83	-0.75	-1.03	-0.87	-0.97	-0.76	-0.62	-0.83
		HFun		0.62	0.80	0.58	0.76	0.78	0.75	0.75	0.74	0.71	0.75	0.56	0.67	
21	44 ¹	UnRlx		0.58	0.74	0.55	0.69	0.70	0.70	0.71	0.67	0.65	0.67	0.52	0.65	
		Rlx	0.62	0.38	0.41	0.39	0.34	0.35	0.37	0.41	0.36	0.34	0.34	0.36	0.50	-0.35
		HFun		0.98	0.99	0.98	1.00	1.00	1.01	1.01	1.00	0.99	1.00	0.97	1.01	
22	27 ¹	UnRlx		0.98	0.99	0.97	0.99	0.99	1.01	1.00	1.00	0.99	0.99	0.96	1.01	
		Rlx	0.38	0.92	1.02	0.90	0.99	1.01	0.98	0.99	0.99	0.96	0.99	0.86	0.97	0.73
		HFun		1.13	1.12	1.13	1.12	1.12	1.15	1.15	1.14	1.14	1.13	1.13	1.18	
23*	44 ⁵	UnRlx		1.13	1.12	1.13	1.12	1.12	1.15	1.15	1.14	1.13	1.13	1.13	1.18	
		Rlx	0.58	1.10	1.21	1.08	1.18	1.21	1.18	1.19	1.19	1.15	1.19	1.04	1.15	0.89
		HFun		-1.87	-1.93	-1.87	-1.92	-1.92	-1.94	-1.95	-1.92	-1.91	-1.92	-1.87	-1.95	
24	58 ³	UnRlx		-1.86	-1.92	-1.87	-1.91	-1.91	-1.94	-1.94	-1.91	-1.90	-1.91	-1.86	-1.95	
		Rlx	0.98	-1.83	-1.89	-1.85	-1.83	-1.81	-1.87	-1.89	-1.83	-1.84	-1.83	-1.82	-1.93	-1.42
		HFun		-1.51	1.64	-1.44	1.57	1.60	1.58	1.63	1.61	1.59	1.60	-1.40	-1.54	
25	25 ⁴	UnRlx		-1.51	1.63	-1.43	1.57	1.60	-1.58	1.63	-1.60	1.58	1.59	-1.38	-1.54	
		Rlx	0.48	-1.37	-1.67	-1.26	-1.46	-1.56	-1.43	-1.53	-1.59	-1.47	-1.54	-1.15	-1.35	-1.24
		HFun		-2.61	1.50	-2.63	-2.58	-2.57	-2.64	-2.60	-2.59	-2.57	1.54	-2.64	-2.71	
26	21 ¹	UnRlx		-2.62	1.48	-2.64	-2.60	-2.59	-2.65	-2.62	-2.62	-2.59	1.53	-2.65	-2.72	
		Rlx	0.49	-2.73	1.79	-2.72	-2.96	-3.15	-2.86	-2.81	-3.03	-2.84	1.84	-2.76	-2.80	-2.05
		HFun		4.20	4.84	4.05	4.75	4.82	4.69	4.69	4.66	4.58	4.69	4.02	4.34	
		UnRlx		4.11	4.74	3.97	4.60	4.65	4.59	4.60	4.51	4.44	4.53	3.91	4.29	

(Continued on next page.)

Table S4: *Continued from previous page.*

Mol. ^{b)}	N_{atom}^{2S+1}	Density ^{c)}	η ^{d)}	DH-1	DH-2	DH-3	DH-4	DH-5	DH-6	DH-7	DH-8	DH-9	DH-10	DH-11	DH-12	Expt.
27	13 ⁶	Rlx	0.00	3.08	2.93	3.12	2.26	1.97	2.68	2.94	1.97	2.46	2.01	2.78	3.52	2.41
		HFun		-0.82	-0.77	-0.83	-0.79	-0.79	-0.80	-0.79	-0.79	-0.79	-0.78	-0.85	-0.83	
		UnRlx		-0.82	-0.78	-0.83	-0.80	-0.80	-0.81	-0.80	-0.80	-0.80	-0.79	-0.85	-0.84	
28	22 ²	Rlx	0.42	-0.86	-0.84	-0.87	-0.90	-0.90	-0.90	-0.86	-0.91	-0.88	-0.89	-0.92	-0.87	-1.23
		HFun		-1.39	-1.50	-1.36	-1.44	-1.46	-1.42	-1.43	-1.42	-1.42	-1.45	-1.30	-1.35	
		UnRlx		-1.39	-1.49	-1.36	-1.45	-1.46	-1.42	-1.44	-1.43	-1.43	-1.45	-1.31	-1.35	
29	51 ²	Rlx	0.49	-1.27	-1.32	-1.25	-1.25	-1.25	-1.25	-1.29	-1.22	-1.26	-1.24	-1.19	-1.27	-1.12
		HFun		0.91	0.95	0.87	0.82	0.81	0.77	0.77	0.84	0.88	0.91	0.78	0.77	
		UnRlx		0.95	1.01	0.91	0.89	0.88	0.83	0.83	0.91	0.93	0.98	0.81	0.79	
30	21 ⁵	Rlx	0.11	0.43	-0.48	0.61	0.45	0.63	0.69	0.69	0.39	0.26	-0.13	0.53	0.66	0.89
		HFun		1.88	1.94	1.86	1.99	1.99	1.99	1.95	1.96	1.94	1.96	1.89	1.93	
		UnRlx		1.90	2.00	1.87	2.05	2.06	2.04	1.99	2.02	1.99	2.02	1.90	1.95	
31	56 ⁵	Rlx	0.13	1.79	1.85	1.77	1.89	1.90	1.91	1.89	1.86	1.85	1.85	1.78	1.88	1.80
		HFun		2.66	2.58	2.55	2.70	2.70	2.70	2.65	2.66	2.64	2.67	2.56	2.62	
		UnRlx		2.71	2.59	2.56	2.75	2.76	2.74	2.69	2.72	2.68	2.72	2.58	2.64	
32	25 ⁵	Rlx	0.34	2.54	2.47	2.45	2.56	2.56	2.58	2.56	2.51	2.51	2.51	2.44	2.56	2.10
		HFun		2.69	2.76	2.67	2.79	2.80	2.79	2.75	2.76	2.74	2.77	2.69	2.73	
		UnRlx		2.70	2.80	2.67	2.84	2.85	2.83	2.79	2.81	2.78	2.82	2.70	2.74	
		Rlx	0.73	2.60	2.65	2.58	2.67	2.67	2.69	2.67	2.62	2.63	2.63	2.58	2.67	2.36
MaxE ^{e)}		HFun		1.79	3.55	1.64	2.81	2.84	2.82	2.87	2.85	2.83	3.59	1.61	1.93	
		UnRlx		1.70	3.53	1.56	2.81	2.84	2.18	2.87	2.10	2.82	3.58	1.50	1.88	
		Rlx		1.18	3.84	1.00	1.36	1.62	1.14	1.15	1.42	1.08	3.89	-0.71	1.11	
MAE ^{e)}		HFun		0.34	0.69	0.32	0.58	0.59	0.59	0.58	0.57	0.56	0.67	0.31	0.37	
		UnRlx		0.34	0.68	0.31	0.48	0.49	0.41	0.48	0.40	0.46	0.57	0.31	0.37	
		Rlx		0.25	0.54	0.23	0.34	0.39	0.31	0.31	0.37	0.31	0.49	0.20	0.28	
MAE ^{f)}		Rlx		0.25	0.40	0.23	0.34	0.39	0.31	0.31	0.37	0.31	0.36	0.20	0.28	

^{a)} The double-hybrid functionals are r^2 SCAN-CIDH (**DH-1**), r^2 SCAN0-2 (**DH-2**), r^2 SCAN-0DH (**DH-3**), B2K-PLYP (**DH-4**), DSD-BLYP (**DH-5**), ω B2GP-PLYP (**DH-6**), RSX-QIDH (**DH-7**), ω PBEP86 (**DH-8**), PBE-QIDH (**DH-9**), DSD-PBEP86 (**DH-10**), PBE-0DH (**DH-11**), and RSX-0DH (**DH-12**).

^{b)} The molecule with an asterisk means that the sign of ΔE_Q is theoretically uncertain and therefore $|\Delta E_Q|$ is used for error analysis.

^{c)} HFun: density of truncated hybrid functional. UnRlx: unrelaxed PT2 density. Rlx: relaxed PT2 density.

^{d)} Calculated by r^2 SCAN-CIDH.

^{e)} Maximum error and mean absolute error. Molecule **15** has been excluded.

^{f)} Mean absolute error of $|\Delta E_Q|$. Molecule **15** has been excluded.

Table S5: ΔE_Q results (in mm/s) of ^{57}Fe by standard and augmented basis functions. ^{a)}

Func. ^{b)}	Mol.	Expt.	S-BAS	A-BAS	Diff.	Mol.	Expt.	S-BAS	A-BAS	Diff.
	13	-1.34				30	1.80			
H-1			-1.594	-1.586	0.008			1.957	1.943	-0.014
H-2			-1.549	-1.530	0.019			1.959	1.954	-0.005
H-3			-1.592	-1.586	0.006			1.886	1.873	-0.013
H-4			-1.545	-1.538	0.007			1.837	1.822	-0.015
H-5			-1.568	-1.563	0.005			1.896	1.879	-0.017
H-6			-1.530	-1.522	0.008			1.675	1.657	-0.018
H-7			-1.566	-1.558	0.008			1.756	1.740	-0.016
H-8			-1.563	-1.555	0.008			1.787	1.772	-0.015
H-9			-1.591	-1.586	0.005			1.869	1.858	-0.011
H-10			-1.563	-1.556	0.007			1.775	1.763	-0.012
H-11			-1.592	-1.584	0.008			1.861	1.847	-0.014
DH-1			-1.684	-1.677	0.007			1.789	1.776	-0.013
DH-2			-2.286	-2.282	0.004			1.853	1.840	-0.013
DH-3			-1.627	-1.619	0.008			1.772	1.758	-0.014
DH-4			-2.429	-2.427	0.002			1.892	1.880	-0.012
DH-5			-2.704	-2.701	0.003			1.901	1.890	-0.011
DH-6			-2.181	-2.179	0.002			1.909	1.897	-0.012
DH-7			-2.095	-2.091	0.004			1.887	1.874	-0.013
DH-8			-2.404	-2.400	0.004			1.856	1.844	-0.012
DH-9			-2.123	-2.119	0.004			1.849	1.837	-0.012
DH-10			-2.459	-2.457	0.002			1.850	1.839	-0.011
DH-11			-1.636	-1.630	0.006			1.781	1.769	-0.012
DH-12			-1.750	-1.742	0.008			1.885	1.871	-0.014

^{a)} The standard basis functions (S-BAS) may be found in the Computational Methods subsection in the main text, whereas in the augmented basis functions (A-BAS) the iron atom are added with two tighter and two more diffuse Gaussian functions with $\alpha_p = 26521.473$, 0.0311738 and $\alpha_d = 6191.1311$, 0.0295094 .

^{b)} The hybrid and double-hybrid functionals have been defined in Tables S3 and S4.