A generally applicable atomic-charge dependent London dispersion correction

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Supplementary Material

Part I: Additional theory, parameters, and timings

A. Classical partial charges

Classical electronegativity equilibration (EEQ) partial charges are determined by minimizing the following energy expression

$$E_{\mathrm{IES}} = \sum_{i=1}^{N} \left(\chi_i q_i + \frac{1}{2} \left(J_{ii} + \frac{2\gamma_{ii}}{\sqrt{\pi}} \right) q_i^2 \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} q_i q_j \frac{\mathrm{erf}(\gamma_{ij} R_{ij})}{R_{ij}} \tag{1}$$

where γ_{ij} is given as $(a_i^2 + a_j^2)^{-\frac{1}{2}}$ with a_i beeing the van der Waals radius of atom i. For a more compact representation we rewrite the above expression in matrix notation

$$E_{\mathrm{IES}} = \mathbf{q}^\top (\frac{1}{2} A\mathbf{q} - \mathbf{X}) \tag{2}$$

where we define the A matrix and the $\mathbf{X}$ vector by

$$X_i = -\chi_i \quad \text{and} \quad A_{ij} = \begin{cases} J_{ii} + \dfrac{\sqrt{2}\gamma_{ii}}{\sqrt{\pi}} & i = j \\ \dfrac{\mathrm{erf}(\gamma_{ij} R_{ij})}{R_{ij}} & \text{otherwise} \end{cases} \tag{3}$$

Note that the choice of $\mathbf{X}$ is defined according to the work of Goedecker *et al.* in 2015 [1], and we keep the original notation to aid comparability. To obtain EEQ partial charges from this equations, under the constraint that the partial charges conserve the total charge q_{total} of the system, the method of constrained Lagrangian optimization is used as

$$L = E_{\mathrm{IES}} + \lambda \left(\sum_{k=1}^{N} q_k - q_{\mathrm{total}} \right) \quad \text{with} \quad \frac{\partial L}{\partial \mathbf{q}} = \mathbf{0} \ \wedge \ \frac{\partial L}{\partial \lambda} = \sum_{i=1}^{N} q_i - q_{\mathrm{total}} = 0 \tag{4}$$

which leads to the following set of $(N+1)$ linear equations

$$\begin{pmatrix} A & \mathbf{1} \\ \mathbf{1}^\top & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{q} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ q_{\mathrm{total}} \end{pmatrix} \tag{5}$$

In contrast to Goedecker's approach we determine χ_i not by a neural network but use a modified variant of the coordination number (mCN) similary as in the DFT-D3 model [2]. For this EEQ charge model we suggest

$$\chi_i = \mathrm{EN}_i - \kappa_i \sqrt{\mathrm{mCN}_i} \tag{6}$$

where EN_i is the electronegativity, κ_i is a scaling factor for the geometry dependency, and mCN_i is the coordination number defined as

$$\mathrm{mCN}_i = \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{2} \cdot \left(1 + \mathrm{erf} \left(-k_1 \cdot \left(\frac{R_{ij}}{R_{ij}^{\mathrm{cov}}} - 1 \right) \right) \right) \tag{7}$$

where k_1 is an ad-hoc parameter which is set to 7.5 to reproduce the short range behaviour of the original DFT-D3 CN as close as possible while having a better long-range behaviour. $R_{ij}^{\mathrm{cov}} = R_i^{\mathrm{cov}} + R_j^{\mathrm{cov}}$ are the covalent radii published by Pyykkö *et al.* in 2010 [3] which are

used to be consistent with the DFT-D3 CN. As we arrived at a stationary point in the constrained optimization we can derive the expression needed to calculate the analytical partial charge derivative by

$$\begin{aligned} \frac{\partial L}{\partial q_k} = 0 \quad \Longrightarrow \quad 0 = \frac{d}{d\mathbf{R}_j}\frac{\partial L}{\partial q_k} = \frac{\partial^2 L}{\partial q_k \partial \mathbf{R}_j} + \frac{\partial^2 L}{\partial q_k^2}\cdot\frac{\partial q_k}{\partial \mathbf{R}_j} \\ \Longleftrightarrow \quad \frac{\partial^2 L}{\partial q_k^2}\cdot\frac{\partial q_k}{\partial \mathbf{R}_j} = -\frac{\partial^2 L}{\partial q_k \partial \mathbf{R}_j} \end{aligned} \tag{8}$$

Plugging in the expression for L from equation 4 we get

$$\frac{\partial^2 L}{\partial \mathbf{R}_j \partial \mathbf{q}} = \begin{pmatrix} \frac{\partial A}{\partial \mathbf{R}_j} & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{q} \\ \lambda \end{pmatrix} + \begin{pmatrix} A & \mathbf{1} \\ \mathbf{1}^\top & 0 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial \mathbf{q}}{\partial \mathbf{R}_j} \\ \frac{\partial \lambda}{\partial \mathbf{R}_j} \end{pmatrix} - \begin{pmatrix} \frac{\partial \mathbf{X}}{\partial \mathbf{R}_j} \\ 0 \end{pmatrix} \tag{9}$$

we do the same to obtain the electronic Hessian from equation 4

$$\frac{\partial^2 L}{\partial \mathbf{q}^2} = \begin{pmatrix} A & \mathbf{1} \\ \mathbf{1}^\top & 0 \end{pmatrix} \tag{10}$$

Plugging everything back into equation 8 we get

$$\begin{pmatrix} \frac{\partial \mathbf{q}}{\partial \mathbf{R}_j} \\ \frac{\partial \lambda}{\partial \mathbf{R}_j} \end{pmatrix} = \begin{pmatrix} A & \mathbf{1} \\ \mathbf{1}^\top & 0 \end{pmatrix}^{-1} \cdot \left(- \begin{pmatrix} \frac{\partial A}{\partial \mathbf{R}_j} & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{q} \\ \lambda \end{pmatrix} + \begin{pmatrix} \frac{\partial \mathbf{X}}{\partial \mathbf{R}_j} \\ 0 \end{pmatrix} \right) \tag{11}$$

To invert the indefinite but symmmetric $(N+1)$ matrix we apply a Bunch–Kaufman factorization. Overall four parameter are fitted for each element i: EN_i, J_{ii}, κ_i, and a_i (namely the atomic electronegativity, atomic hardness terms, element specific scaling parameters, and atomic van der Waals radii).

Table A1: Atomic electronegativities EN, element-dependent atomic hardness terms J, element specific scaling parameters κ, and atomic van der Waals radii a for all elements up to radon ($Z = 86$).

Atomic number	EN_i	J_{ii}	κ_i	a_i
1	1.23695041	-0.35015861	0.04916110	0.55159092
2	1.26590957	1.04121227	0.10937243	0.66205886
3	0.54341808	0.09281243	-0.12349591	0.90529132
4	0.99666991	0.09412380	-0.02665108	1.51710827
5	1.26691604	0.26629137	-0.02631658	2.86070364
6	1.40028282	0.19408787	0.06005196	1.88862966
7	1.55819364	0.05317918	0.09279548	1.32250290
8	1.56866440	0.03151644	0.11689703	1.23166285
9	1.57540015	0.32275132	0.15704746	1.77503721
10	1.15056627	1.30996037	0.07987901	1.11955204
11	0.55936220	0.24206510	-0.10002962	1.28263182
12	0.72373742	0.04147733	-0.07712863	1.22344336
13	1.12910844	0.11634126	-0.02170561	1.70936266

Table A1: Atomic electronegativities EN, element-dependent atomic hardness terms J, element specific scaling parameters κ, and atomic van der Waals radii a for all elements up to radon ($Z = 86$).

Atomic number	EN_i	J_{ii}	κ_i	a_i
14	1.12306840	0.13155266	-0.04964052	1.54075036
15	1.52672442	0.15350650	0.14250599	1.38200579
16	1.40768172	0.15250997	0.07126660	2.18849322
17	1.48154584	0.17523529	0.13682750	1.36779065
18	1.31062963	0.28774450	0.14877121	1.27039703
19	0.40374140	0.42937314	-0.10219289	1.64466502
20	0.75442607	0.01896455	-0.08979338	1.58859404
21	0.76482096	0.07179178	-0.08273597	1.65357953
22	0.98457281	-0.01121381	-0.01754829	1.50021521
23	0.96702598	-0.03093370	-0.02765460	1.30104175
24	1.05266584	0.02716319	-0.02558926	1.46301827
25	0.93274875	-0.01843812	-0.08010286	1.32928147
26	1.04025281	-0.15270393	-0.04163215	1.02766713
27	0.92738624	-0.09192645	-0.09369631	1.02291377
28	1.07419210	-0.13418723	-0.03774117	0.94343886
29	1.07900668	-0.09861139	-0.05759708	1.14881311
30	1.04712861	0.18338109	0.02431998	1.47080755
31	1.15018618	0.08299615	-0.01056270	1.76901636
32	1.15388455	0.11370033	-0.02692862	1.98724061
33	1.36313743	0.19005278	0.07657769	2.41244711
34	1.36485106	0.10980677	0.06561608	2.26739524
35	1.39801837	0.12327841	0.08006749	2.95378999
36	1.18695346	0.25345554	0.14139200	1.20807752
37	0.36273870	0.58615231	-0.05351029	1.65941046
38	0.58797255	0.16093861	-0.06701705	1.62733880
39	0.71961946	0.04548530	-0.07377246	1.61344972
40	0.96158233	-0.02478645	-0.02927768	1.63220728
41	0.89585296	0.01909943	-0.03867291	1.60899928
42	0.81360499	0.01402541	-0.06929825	1.43501286
43	1.00794665	-0.03595279	-0.04485293	1.54559205
44	0.92613682	0.01137752	-0.04800824	1.32663678
45	1.09152285	-0.03697213	-0.01484022	1.37644152
46	1.14907070	0.08009416	0.07917502	1.36051851
47	1.13508911	0.02274892	0.06619243	1.23395526
48	1.08853785	0.12801822	0.02434095	1.65734544
49	1.11005982	-0.02078702	-0.01505548	1.53895240
50	1.12452195	0.05284319	-0.03030768	1.97542736
51	1.21642129	0.07581190	0.01418235	1.97636542
52	1.36507125	0.09663758	0.08953411	2.05432381
53	1.40340000	0.09547417	0.08967527	3.80138135
54	1.16653482	0.07803344	0.07277771	1.43893803
55	0.34125098	0.64913257	-0.02129476	1.75505957
56	0.58884173	0.15348654	-0.06188828	1.59815118
57	0.68441115	0.05054344	-0.06568203	1.76401732

Table A1: Atomic electronegativities EN, element-dependent atomic hardness terms J, element specific scaling parameters κ, and atomic van der Waals radii a for all elements up to radon ($Z = 86$).

Atomic number	EN_i	J_{ii}	κ_i	a_i
58	0.56999999	0.11000000	-0.11000000	1.63999999
59	0.56999999	0.11000000	-0.11000000	1.63999999
60	0.56999999	0.11000000	-0.11000000	1.63999999
61	0.56999999	0.11000000	-0.11000000	1.63999999
62	0.56999999	0.11000000	-0.11000000	1.63999999
63	0.56999999	0.11000000	-0.11000000	1.63999999
64	0.56999999	0.11000000	-0.11000000	1.63999999
65	0.56999999	0.11000000	-0.11000000	1.63999999
66	0.56999999	0.11000000	-0.11000000	1.63999999
67	0.56999999	0.11000000	-0.11000000	1.63999999
68	0.56999999	0.11000000	-0.11000000	1.63999999
69	0.56999999	0.11000000	-0.11000000	1.63999999
70	0.56999999	0.11000000	-0.11000000	1.63999999
71	0.56999999	0.11000000	-0.11000000	1.63999999
72	0.87936784	-0.02786741	-0.03585873	1.47055223
73	1.02761808	0.01057858	-0.03132400	1.81127084
74	0.93297476	-0.03892226	-0.05902379	1.40189963
75	1.10172128	-0.04574364	-0.02827592	1.54015481
76	0.97350071	-0.03874080	-0.07606260	1.33721475
77	1.16695666	-0.03782372	-0.02123839	1.57165422
78	1.23997927	-0.07046855	0.03814822	1.04815857
79	1.18464453	0.09546597	0.02146834	1.78342098
80	1.14191734	0.21953269	0.01580538	2.79106396
81	1.12334192	0.02522348	-0.00894298	1.78160840
82	1.01485321	0.15263050	-0.05864876	2.47588882
83	1.12950808	0.08042611	-0.01817842	2.37670734
84	1.30804834	0.01878626	0.07721851	1.76613217
85	1.33689961	0.08715453	0.07936083	2.66172302
86	1.27465977	0.10500484	0.05849285	2.82773085

The quality of those classical partial charges can be seen in Figure 1 and in Figure 2 where we correlate PBE0/def2-TZVP Hirshfeld partial charges with classical EEQ charges and with GFN2-xTB charges. As can be seen from the Table A2, GFN2-xTB converges in some cases to the wrong electronic solution, so that huge deviations can occur (maximum deviation is 19.92 e^-). The EEQ model on the other hand proves to be quite robust and can convince with a maximum deviation of 0.56 e^- on more than 20000 calculated data points for the $Z = 1 - 86$ case.

Table A2: Statistical measures calculated for the comparison between calculated partial charges and reference PBE0/def2-TZVP Hirshfeld partial charges. Deviations are given in e^-.

Measure	EEQ($Z = 1 - 86$)	GFN2-xTB($Z = 1 - 86$)	EEQ($Z = 1 - 17$)	GFN2-xTB($Z = 1 - 17$)
MAD	0.04	0.13	0.03	0.18
MD	0.00	0.00	0.00	-0.01
SD	0.06	0.36	0.05	0.65
AMAX	0.56	19.27	0.33	19.92

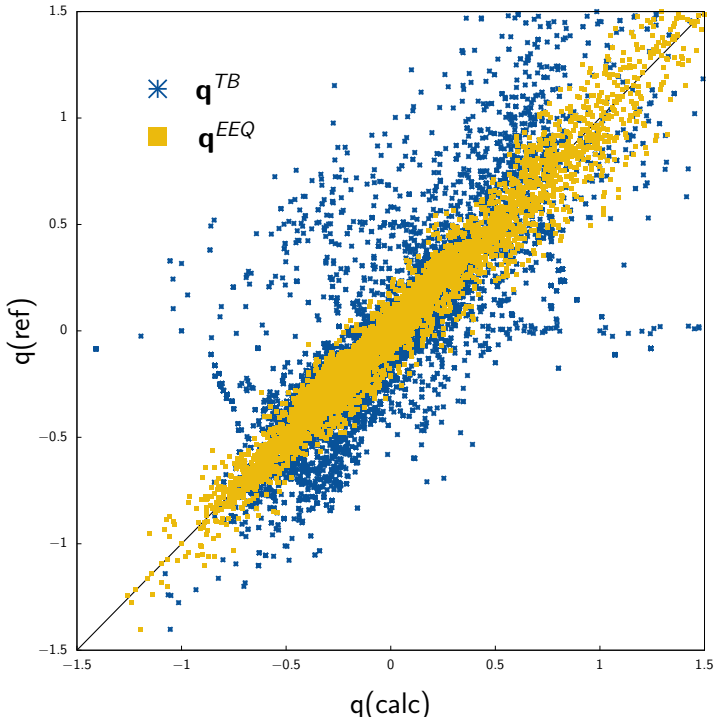

Figure 1: EEQ versus GFN2-xTB partial charges in direct correlation with Hirshfeld partial charges calculated at the PBE0/def2-TZVP level of theory for all elements with $Z = 1 - 86$.

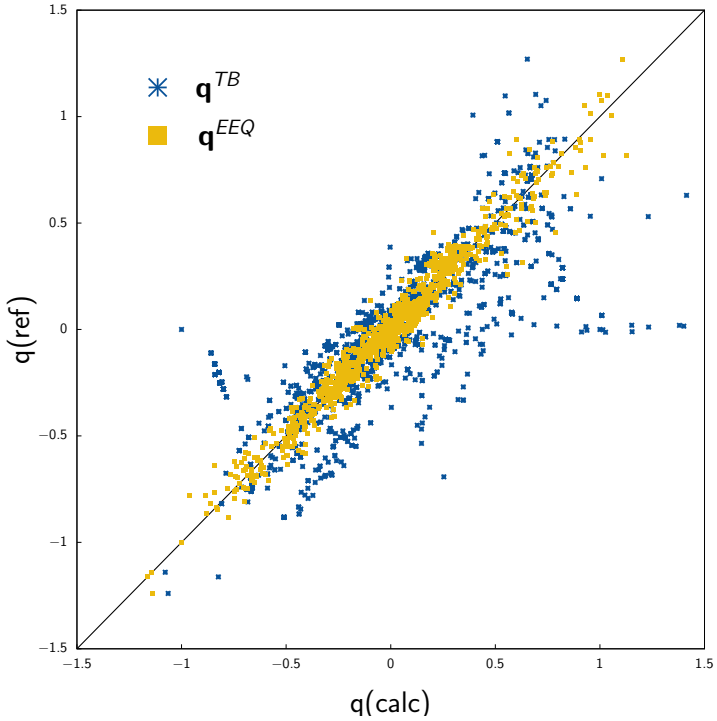

Figure 2: EEQ versus GFN2-xTB partial charges in direct correlation with Hirshfeld partial charges calculated at the PBE0/def2-TZVP level of theory for all elements with $Z = 1 - 17$ (excluding helium and neon).

B. Many-body dispersion theory

Tkatchenko et al. [4] have shown that the dispersion energy can be written as

$$E_{\text{disp}}^{(n),MBD} = \int_0^\infty \frac{d\omega}{2\pi} \, \mathbf{Tr} \left\{ \ln \left(\mathbf{1} - \mathbf{A}(i\omega)\mathbf{T} \right) \right\}, \tag{12}$$

when neglecting intra-oscillator interactions [5] within the matrix formulation $\big(\mathbf{Tr} \left\{ \mathbf{A}(i\omega)\mathbf{T} \right\} = 0 \big)$. In DFT-D4, the frequency-dependent polarizability matrix $\mathbf{A}(i\omega)$ is obtained from the previously generated atom-in-molecule dynamic polarizabilities

$$\begin{aligned} A_{KP}^{\beta\gamma}(i\omega) &= \alpha^K(i\omega)\delta_{KP}\delta_{\gamma\beta} \\ &= \alpha^K(i\omega, z^K, CN^K)\, \delta_{KP}\, \delta_{\gamma\beta}. \end{aligned} \tag{13}$$

In equation 13, K and P label atoms, and β and γ refer to the Cartesian components of their internuclear distance. The use of D4 atom-in-molecule dynamic polarizabilities offers advantages. Different from the TS-based polarizabilites, the D4 polarizabilites already contain information about the molecular environment and no self-consistent screening needs to be performed, which can jeopardize the stability of the method [6]. The generation of the D4 polarizabilities is simple and robust, since only the geometry and atomic partial charges are needed and no additional information from DFT is required. $\mathbf{T}$ is the interaction tensor describing the coupling between the oscillators. The matrix elements of the damped interaction tensor $\mathbf{T}$ are given by

$$T_{KP}^{\beta\gamma} = \sqrt{f_{\text{BJD}}^{(6)}} \frac{\partial}{\partial R_{KP}^{\beta}} \frac{\partial}{\partial R_{KP}^{\gamma}} \left(\frac{1}{R_{KP}} \right). \tag{14}$$

It should be noted that the BJ-damping function is used here as well to screen the elements of the tensor. A motivation for this choice is given below. The MBD energy can be viewed as a series of n-body dipole-dipole terms, and hence, the n-body energy can be obtained directly *via* a Casimir-Polder similar integration of the coupled atom-in-molecule polarizabilities. Because the contributions of the terms in the series tend to oscillate and it converges slowly with n, the value of the limit of the series is used here as computed in equation 12. The astute reader will note that the evaluation of the logarithmic trace in equation 12 is not directly possible since the product $\mathbf{A}(i\omega)\mathbf{T}$ is a trace-less matrix. To obtain the logarithmic trace, the matrix created by subtraction $(\mathbf{1} - \mathbf{A}(i\omega)\mathbf{T})$ is diagonalized and the sum of the eigenvalues is used to calculate all many-body dispersion terms. Furthermore, splitting the diagonal polarizability matrix $\mathbf{A}(i\omega)$ into the product of its square roots, which is possible due to the invariance regarding cyclic permutation, simplifies the problem to symmetrical matrices only, which makes the calculation of eigenvalues much simpler

$$\left(\mathbf{1} - \mathbf{A}^{1/2}(i\omega)\mathbf{T}\mathbf{A}^{1/2}(i\omega) \right) \mathbf{U} = \mathbf{U}\mathbf{\Lambda}. \tag{15}$$

Here, $\mathbf{\Lambda}$ represents the matrix of eigenvalues with elements λ. The eigenvalues are then used analogously to equation 12, and hence the final expression for the MBD energy reads

$$E_{disp}^{(n),MBD} = \int_0^\infty \frac{d\omega}{2\pi} \, \ln \left(\prod_{l=1}^{3N} \lambda_l \right). \tag{16}$$

Semi-local DFAs already include short-ranged electron correlation within the exchange-correlation functional. Along with avoiding singularities, this is why the dispersion energy is always damped

at short range. Likewise, the interaction tensor in the MBD model needs to be damped. Ideally, the second order term of the MBD energy should be exactly equivalent to the D4 two-body dipole-dipole energy, i.e.,

$$\begin{aligned}
E_{\text{disp}}^{(6),MBD} &= -\int_0^\infty \frac{d\omega}{2\pi}\,\mathbf{Tr}\left\{\frac{1}{2}\left(\mathbf{A}(i\omega)\mathbf{T}\right)^2\right\} \\
&= -\int_0^\infty \frac{d\omega}{2\pi}\,\frac{1}{2}\sum_K^N\sum_P^N \frac{\alpha^K(i\omega)\alpha^P(i\omega)}{R_{KP}^{10}} f_{damp}^2 \\
&\times \sum_\beta^3\sum_\gamma^3 \left(3R_{KP}^\beta R_{KP}^\gamma - \delta_{\beta\gamma}R_{KP}^2\right)^2 \qquad (17)\\
&= -\frac{1}{2}\sum_K^N\sum_P^N \frac{C_6^{KP}}{R_{KP}^6} f_{damp}^2 \\
&\stackrel{!}{=} -\frac{1}{2}\sum_K^N\sum_P^N \frac{C_6^{KP}}{R_{KP}^6} f_{BJD}^{(6)} = E_{disp}^{(6)}.
\end{aligned}$$

Hence, the square root of the BJ-damping function is used to damp the MBD interaction tensor. Nevertheless, it should be noted that for higher interaction orders (higher exponentiation of f_{damp}), the respective MBD energy contributions become damped more strongly also in the mid-range distance regime. However, this peculiarity is considered to be small, since the higher-order ($n > 2$) MBD energies represent a smaller fraction of the total dispersion energy (usually one to two magnitudes less than two-body contributions).

The final D4-MBD dispersion energy expression consists of two parts. The first compose the two-body dipole-dipole and dipole-quadrupole interaction (denoted as $E_{disp}^{(6,8)}$). The second part includes all dipole-dipole interactions up to infinite order, $E_{disp}^{(n),MBD}$ ($n = 6, 9, 12, 15, \ldots, \infty$). To avoid double counting of the two-body dipole-dipole energy, it is removed explicitly from the MBD energy according to

$$E_{disp}^{D4-MBD} = E_{disp}^{(6,8)} + \left(E_{disp}^{(n),MBD} - E_{disp}^{(6),MBD}\right). \qquad (18)$$

Exploiting that $E_{disp}^{(6)} = E_{disp}^{(6),MBD}$ and re-arranging to $E_{disp}^{D4-MBD} = E_{disp}^{(n),MBD} + E_{disp}^{(8)}$ is not possible in the general case, as for double hybrid density functionals (abbreviated as DHDF) $s_6 \neq 1$, whereas this scaling cannot be applied to an individual term in the infinite-order MBD energy. Hence, the dispersion energy in DFT-D4-MBD is always calculated as shown in Eq. 18.

Similar to Figure 16 of Ref.[7], the contributions to the dispersion energy considered in D4 are put into context with other correction schemes in Figure 3.

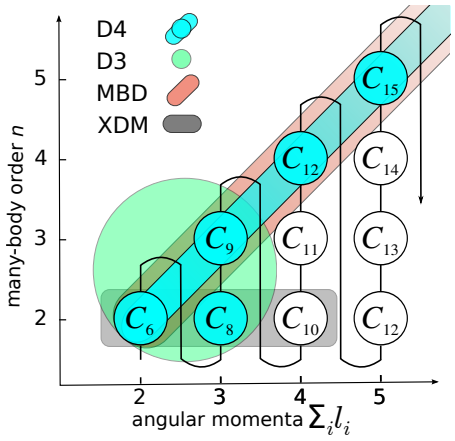

Figure 3: Asymptotic dispersion coefficients from different many-body orders and increasing number of terms in the multipole expansion. The contributions covered by the D3 (including ATM term), D4-MBD, MBD, and XDM methods are highlighted. This Figure is generated in analogy to Figure 16 in Ref.[7].

C. Tight-binding two–body dispersion potential (GFN2-xTB)

We developed the GFN2-xTB dispersion potential in terms of density fluctuations (see Ref. [8])

$$\frac{\partial}{\partial c_{\nu i}}\left[E_{\mathrm{disp}}^{(6,8)}-\sum_j n_j\varepsilon_j\left(\sum_{A,B}\sum_{\kappa\in A}\sum_{\lambda\in B}c_{\kappa j}c_{\lambda j}S_{\kappa\lambda}-1\right)\right]=0$$

Take the derivative of $E_{disp}^{(6,8)}$ with respect to the AO coefficient

$$\begin{aligned}
\frac{\partial E_{\mathrm{disp}}^{(6,8)}}{\partial c_{\nu i}} &= \frac{\partial}{\partial c_{\nu i}}\frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\underbrace{\zeta(z^A,z^{A,ref})}_{\zeta_A^{A,ref}}\underbrace{\zeta(z^B,z^{B,ref})}_{\zeta_B^{B,ref}}W_A^{A,ref}W_B^{B,ref}\\
&\quad\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&= \frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_A^{A,ref}}{\partial c_{\nu i}}\zeta_B^{B,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&\quad+\frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_B^{B,ref}}{\partial c_{\nu i}}\zeta_A^{A,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&= \frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\sum_D\frac{\partial\zeta_A^{A,ref}}{\partial q_D}\frac{\partial q_D}{\partial c_{\nu i}}\zeta_B^{B,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&\quad+\frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\sum_D\frac{\partial\zeta_B^{B,ref}}{\partial q_D}\frac{\partial q_D}{\partial c_{\nu i}}\zeta_A^{A,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&= \frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_A^{A,ref}}{\partial q_A}\frac{\partial q_A}{\partial c_{\nu i}}\zeta_B^{B,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&\quad+\frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_B^{B,ref}}{\partial q_B}\frac{\partial q_B}{\partial c_{\nu i}}\zeta_A^{A,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&= \frac{1}{2}\sum_A\sum_{A,ref}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_A^{A,ref}}{\partial q_A}\left(\delta_{AD}\sum_C\sum_{\kappa\in C}n_ic_{\kappa i}S_{\nu\kappa}+\sum_{\mu\in A}n_ic_{\mu i}S_{\nu\mu}\right)\zeta_B^{B,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&\quad+\frac{1}{2}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\frac{\partial\zeta_B^{B,ref}}{\partial q_B}\left(\delta_{BD}\sum_C\sum_{\kappa\in C}n_ic_{\kappa i}S_{\nu\kappa}+\sum_{\mu\in A}n_ic_{\mu i}S_{\nu\mu}\right)\zeta_A^{A,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\\
&= \frac{1}{2}\sum_{D,ref=1}^{N^{D,ref}}\frac{\partial\zeta_D^{D,ref}}{\partial q_D}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\zeta_B^{B,ref}W_D^{D,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{DB}}{R_{DB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\sum_C\sum_{\kappa\in C}n_ic_{\kappa i}S_{\nu\kappa}\\
&\quad+\frac{1}{2}\sum_{D,ref=1}^{N^{D,ref}}\frac{\partial\zeta_D^{d}}{\partial q_D}\sum_A\sum_{A,ref=1}^{N^{A,ref}}\zeta_A^{A,ref}W_A^{A,ref}W_D^{D,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AD}}{R_{AD}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})\sum_C\sum_{\kappa\in C}n_ic_{\kappa i}S_{\nu\kappa}
\end{aligned}$$

$$\frac{\partial E_{\mathrm{disp}}^{(6,8)}}{\partial c_{\nu i}}=\underbrace{\sum_{A,ref=1}^{N^{A,ref}}\frac{\partial\zeta_A^{A,ref}}{\partial q_A}\sum_B\sum_{B,ref=1}^{N^{B,ref}}\zeta_B^{B,ref}W_A^{A,ref}W_B^{B,ref}\sum_{n=6,8}s_n\frac{C_{(n)}^{AB}}{R_{AB}^{(n)}}f_{\mathrm{BJD}}^{(n)}(R_{AB})}_{d_A}\sum_C\sum_{\kappa\in C}n_ic_{\kappa i}S_{\nu\kappa}$$

Which leads to the two–body DFT–D4 potential used within the GFN2-xTB method

$$F_{\kappa\lambda}^{\mathrm{D4}}=\frac{1}{2}S_{\kappa\lambda}(d_A+d_B),\forall\kappa\in A,\lambda\in B$$

D. Double hybrid density functionals

In the following we give the construction scheme to build the double hybrid density functionals (DHDF) as

$$E_{\mathrm{DHDF}} = (1 - a_x^{\mathrm{Fock}})E_x^{\mathrm{DFT}} + a_x^{\mathrm{Fock}} + a_c^{\mathrm{DFT}}E_c^{\mathrm{DFT}} + a_c^{\mathrm{PT2,\,OS}}E_{c,\mathrm{OS}}^{\mathrm{PT2}} + a_c^{\mathrm{PT2,\,SS}}E_{c,\mathrm{SS}}^{\mathrm{PT2}}.$$

Table A3: Double hybrid functional definitions as given in the literature.

Name	Exchange	Correlation	a_x^{Fock}	a_c^{DFT}	$a_c^{\mathrm{PT2,\,OS}}$	$a_c^{\mathrm{PT2,\,SS}}$	Ref.
B2PLYP	B88	LYP	0.5300	0.7300	0.2700	0.2700	[9]
mPW2PLYP	mPW	LYP	0.5500	0.7500	0.2500	0.2500	[10]
PWPB95	PW	B95	0.5000	0.7310	0.2690	0.0000	[11]
DSD-BLYP	B88	LYP	0.6900	0.5400	0.4600	0.3700	[12]
DSD-PBE	PBE	PBE	0.6800	0.4900	0.5500	0.1300	[13]
DSD-PBEB95	PBE	B95	0.6600	0.5500	0.4600	0.0900	[13]
DSD-PBEP86	PBE	P86	0.7000	0.4300	0.5300	0.2500	[13]
DSD-SVWN	Slater	VWN5	0.7200	0.3300	0.5900	0.1200	[13]
DOD-BLYP	B88	LYP	0.6500	0.5800	0.5300	0.0000	[13]
DOD-PBE	PBE	PBE	0.6400	0.5400	0.4200	0.0000	[13]
DOD-PBEB95	PBE	B95	0.6400	0.5700	0.4600	0.0000	[13]
DOD-PBEP86	PBE	P86	0.6500	0.4700	0.5400	0.0000	[13]
DOD-SVWN	Slater	VWN5	0.6900	0.3400	0.5800	0.0000	[13]
PBE0-2	PBE	PBE	0.7937	0.5000	0.5000	0.5000	[14]
PBE0-DH	PBE	PBE	0.5000	0.8750	0.1250	0.1250	[15]

Within this section we neglect explicit notation for EEQ charges and denote GFN2-xTB Mulliken-type charges as "TB".

E. BJ-damping parameters

Different parametrizations are created for the application of either ATM or MBD for higher-order dipole-dipole interactions within the DFT-D4 treatment.

Table A4: BJ-damping parameter (DFT-D4-ATM, **default model** also abbreviated as DFT-D4) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
B1B95	1.0000	1.277 011 62	0.405 547 15	4.633 230 74
B1LYP	1.0000	1.985 537 11	0.393 090 40	4.554 651 45
B1P	1.0000	3.361 150 15	0.486 652 93	5.052 195 72
B1PW	1.0000	3.022 275 50	0.473 968 46	4.498 453 09
B2PLYP	0.6400	1.168 886 46	0.441 546 04	4.731 146 42
B3LYP	1.0000	2.029 293 67	0.408 680 35	4.538 071 37
B3P	1.0000	3.088 221 55	0.473 242 38	4.986 821 34
B3PW	1.0000	2.883 642 95	0.469 908 60	4.516 414 22
B97	1.0000	0.878 542 60	0.293 191 26	4.516 477 19
BHLYP	1.0000	1.652 816 46	0.272 636 60	5.486 345 86
BLYP	1.0000	2.340 766 71	0.444 888 65	4.093 300 90
BPBE	1.0000	3.644 052 46	0.529 056 20	4.113 118 91
BP	1.0000	3.354 979 27	0.436 458 61	4.924 068 54
BPW	1.0000	3.245 715 06	0.500 504 54	4.123 464 83
CAMB3LYP	1.0000	1.660 413 01	0.402 671 56	5.174 321 95
DODBLYP	0.4700	1.311 460 43	0.434 072 94	4.279 143 60
DODPBEB95	0.5600	0.015 746 35	0.437 457 20	3.691 807 63
DODPBE	0.4800	0.920 514 54	0.430 370 52	4.380 672 38
DODPBEP86	0.4600	0.714 056 81	0.424 086 65	4.528 844 39
DODSVWN	0.4200	0.945 002 07	0.474 490 26	5.053 160 93
DSDBLYP	0.5400	0.630 182 37	0.475 918 35	4.737 137 81
DSDPBEB95	0.5400	−0.146 686 70	0.463 945 87	3.649 138 60
DSDPBE	0.4500	0.705 841 16	0.457 870 85	4.445 667 42
DSDPBEP86	0.4700	0.375 866 75	0.536 987 68	5.130 224 35
DSDSVWN	0.4100	0.729 144 36	0.513 474 12	5.118 585 41
GLYP	1.0000	4.237 989 24	0.384 264 65	4.384 128 63
HF	1.0000	1.616 798 27	0.449 592 24	3.357 436 05
LB94	1.0000	2.595 384 99	0.420 889 44	3.281 932 23
LCBLYP	1.0000	1.603 441 80	0.457 698 39	7.869 248 93
Lh07s-SVWN	1.0000	3.166 755 31	0.359 655 52	4.319 476 14
Lh07t-SVWN	1.0000	2.093 330 01	0.350 251 89	4.341 665 15
Lh12ct-SsifPW92	1.0000	2.684 676 10	0.341 904 16	3.910 396 66
Lh12ct-SsirPW92	1.0000	2.489 734 02	0.340 260 75	3.969 480 81
Lh14t-calPBE	1.0000	1.281 307 70	0.388 220 21	4.925 012 11
M06	1.0000	0.163 667 29	0.534 564 13	6.061 921 74

Table A4: BJ-damping parameter (DFT-D4-ATM, **default model** also abbreviated as DFT-D4) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
M06L	1.0000	0.594 937 60	0.714 223 59	6.353 141 82
mPW1B95	1.0000	0.500 930 24	0.415 850 97	4.991 548 69
mPW1LYP	1.0000	1.155 911 53	0.256 034 93	5.320 838 95
mPW1PW	1.0000	1.808 417 16	0.429 618 19	4.688 923 41
mPW2PLYP	0.7500	0.457 888 46	0.429 977 04	5.076 506 82
mPWB1K	1.0000	0.573 383 13	0.446 879 75	5.212 667 77
mPWLYP	1.0000	1.258 429 42	0.257 738 94	5.023 195 42
mPWPW	1.0000	1.825 968 36	0.345 267 45	4.846 207 34
O3LYP	1.0000	1.757 625 08	0.103 489 80	6.162 332 82
OLYP	1.0000	2.748 368 20	0.601 844 98	2.532 921 67
OPBE	1.0000	3.069 174 17	0.682 675 34	2.228 490 18
PBE0-2	0.5000	0.642 990 82	0.765 421 15	5.785 786 75
PBE0	1.0000	1.200 654 98	0.400 855 97	5.029 287 89
PBE0-DH	0.8750	0.968 115 78	0.475 924 88	5.086 228 73
PBE	1.0000	0.959 480 85	0.385 749 91	4.806 885 34
PW1PW	1.0000	0.968 501 70	0.424 275 11	5.020 606 36
PW6B95	1.0000	−0.319 260 54	0.041 429 19	5.846 556 08
PW86PBE	1.0000	1.213 628 56	0.405 103 66	4.667 377 24
PW91	1.0000	0.772 831 11	0.395 815 42	4.934 057 61
PWP1	1.0000	0.604 925 65	0.468 558 37	5.769 214 13
PWPB95	0.8200	−0.346 391 27	0.410 806 36	3.838 782 74
PWP	1.0000	0.328 012 27	0.358 746 87	6.058 611 68
revPBE0	1.0000	1.571 854 14	0.387 059 66	4.110 288 76
revPBE0-DH	0.8750	1.244 560 37	0.367 305 60	4.711 264 82
revPBE38	1.0000	1.665 974 72	0.394 768 33	4.390 266 28
revPBE	1.0000	1.746 765 30	0.536 349 00	3.072 614 85
revTPSS0	1.0000	1.546 644 99	0.458 909 64	4.784 264 05
revTPSS	1.0000	1.530 894 54	0.448 805 97	4.640 423 17
revTPSSH	1.0000	1.527 403 07	0.451 619 57	4.707 794 83
RPBE	1.0000	1.311 837 87	0.461 694 93	3.157 117 57
RPW86PBE	1.0000	1.126 240 34	0.381 512 18	4.754 804 72
SCAN	1.0000	1.461 260 56	0.629 308 55	6.312 840 39
TPSS0	1.0000	1.624 381 02	0.403 290 22	4.805 378 71
TPSS	1.0000	1.765 963 55	0.428 223 03	4.542 571 02
TPSSH	1.0000	1.858 977 50	0.442 869 66	4.602 305 34
ωB97	1.0000	6.557 925 98	0.766 668 02	8.360 273 34
ωB97X	1.0000	−0.075 195 16	0.450 948 93	6.784 252 55
X3LYP	1.0000	1.547 014 29	0.203 184 43	5.618 526 48
XLYP	1.0000	1.629 720 54	0.112 686 73	5.407 864 17

Table A5: BJ-damping parameter (DFT-D4-MBD) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
B1B95	1.0000	1.195 494 20	0.392 414 74	4.603 976 11
B1LYP	1.0000	1.946 095 14	0.386 433 51	4.541 359 68
B1P	1.0000	3.386 930 11	0.484 786 15	5.043 612 24
B1PW	1.0000	2.984 022 04	0.468 629 50	4.486 378 49
B2PLYP	0.6400	1.151 177 73	0.426 661 67	4.736 357 90
B3LYP	1.0000	2.002 462 46	0.402 761 91	4.527 783 20
B3P	1.0000	3.144 562 98	0.471 879 47	4.986 242 58
B3PW	1.0000	2.856 562 68	0.464 918 01	4.506 014 52
B97	1.0000	0.811 712 11	0.284 612 83	4.486 914 68
BHLYP	1.0000	1.680 829 73	0.268 358 37	5.488 472 18
BLYP	1.0000	2.339 713 06	0.447 336 88	4.065 839 31
BPBE	1.0000	3.653 229 96	0.499 335 01	4.242 948 52
BP	1.0000	3.337 281 76	0.432 203 30	4.914 430 61
BPW	1.0000	3.231 374 32	0.499 552 26	4.104 110 84
CAMB3LYP	1.0000	1.744 079 61	0.401 378 70	5.187 312 25
DODBLYP	0.4700	1.178 099 56	0.402 524 28	4.250 965 55
DODPBEB95	0.5400	−0.157 028 03	0.306 293 89	3.691 709 56
DODPBE	0.4800	0.839 083 32	0.406 559 01	4.336 012 39
DODPBEP86	0.4600	0.683 099 10	0.406 009 75	4.500 117 72
DODSVWN	0.4200	1.018 903 45	0.461 674 59	5.111 213 82
DSDBLYP	0.5400	0.654 388 17	0.465 495 74	4.734 498 99
DSDPBEB95	0.5400	−0.243 368 62	0.326 974 09	3.697 675 40
DSDPBE	0.4500	0.661 167 83	0.435 659 15	4.411 106 70
DSDPBEP86	0.4700	0.511 578 21	0.538 897 89	5.186 459 43
DSDSVWN	0.4100	0.900 844 57	0.511 065 29	5.224 901 48
GLYP	1.0000	3.838 615 84	0.363 439 54	4.328 751 83
HF	1.0000	1.460 011 46	0.431 869 01	3.341 160 14
LB94	1.0000	2.364 615 24	0.415 183 79	3.193 654 71
LCBLYP	1.0000	2.401 099 62	0.478 674 38	8.010 384 24
Lh07s-SVWN	1.0000	2.924 984 06	0.341 739 88	4.284 049 51
Lh07t-SVWN	1.0000	1.953 893 00	0.335 115 15	4.318 539 58
Lh12ct-SsifPW92	1.0000	2.413 566 07	0.313 913 16	3.889 357 69
Lh12ct-SsirPW92	1.0000	2.249 171 62	0.314 465 75	3.950 709 25
Lh14t-calPBE	1.0000	1.276 772 53	0.381 286 70	4.916 988 83
M06	1.0000	0.229 482 74	0.529 272 85	6.065 167 82
M06L	1.0000	0.400 777 79	0.696 114 05	6.290 920 87
mPW1B95	1.0000	0.537 918 35	0.410 169 13	4.992 841 76
mPW1LYP	1.0000	1.199 861 00	0.255 024 69	5.323 013 04
mPW1PW	1.0000	1.806 569 73	0.424 569 67	4.681 323 17
mPW2PLYP	0.7500	0.611 611 79	0.437 483 16	5.125 403 64
mPWB1K	1.0000	0.622 211 46	0.442 167 45	5.213 246 59
mPWLYP	1.0000	1.182 433 37	0.389 689 85	4.308 352 85
mPWPW	1.0000	1.796 740 14	0.338 704 79	4.834 422 13
O3LYP	1.0000	1.777 938 02	0.099 617 45	6.160 893 04
OLYP	1.0000	2.587 170 41	0.597 592 71	2.487 603 53

Table A5: BJ-damping parameter (DFT-D4-MBD) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
OPBE	1.0000	2.935 441 02	0.679 039 33	2.198 100 71
PBE0-2	0.5000	0.988 348 59	0.779 110 62	5.903 895 69
PBE0	1.0000	1.268 294 75	0.399 070 98	5.039 513 04
PBE0-DH	0.8750	1.193 060 02	0.461 067 84	5.252 104 80
PBE	1.0000	0.999 246 14	0.381 425 28	4.818 392 84
PW1PW	1.0000	1.097 590 50	0.427 598 30	5.045 595 72
PW6B95	1.0000	−0.316 299 35	0.039 993 57	5.836 902 54
PW86PBE	1.0000	1.228 429 87	0.399 988 24	4.667 391 11
PW91	1.0000	0.814 068 82	0.340 947 06	5.185 688 23
PWP1	1.0000	0.959 362 22	0.485 529 82	5.849 564 11
PWPB95	0.8200	−0.464 537 80	0.298 841 36	3.876 412 55
PWP	1.0000	0.660 560 55	0.377 680 52	6.147 871 38
revPBE0	1.0000	1.471 982 56	0.374 717 56	4.089 043 69
revPBE0-DH	0.8750	1.224 941 88	0.359 047 81	4.702 160 12
revPBE38	1.0000	1.604 235 29	0.389 384 75	4.355 578 32
revPBE	1.0000	1.625 436 93	0.540 318 31	2.979 656 48
revTPSS0	1.0000	1.553 218 88	0.453 553 19	4.775 885 98
revTPSS	1.0000	1.518 580 35	0.442 432 22	4.628 816 20
revTPSSH	1.0000	1.525 420 64	0.445 702 07	4.698 837 17
RPBE	1.0000	1.117 936 96	0.446 324 88	3.088 909 17
RPW86PBE	1.0000	1.137 958 71	0.376 365 36	4.752 363 84
SCAN	1.0000	1.754 083 15	0.635 713 34	6.356 907 48
TPSS0	1.0000	1.667 526 98	0.400 747 46	4.809 271 96
TPSS	1.0000	1.911 308 49	0.433 328 51	4.569 867 97
TPSSH	1.0000	1.887 835 25	0.439 681 67	4.603 427 00
ωB97	1.0000	7.110 224 68	0.764 233 45	8.445 593 34
ωB97X	1.0000	0.388 153 38	0.474 486 29	6.913 673 84
X3LYP	1.0000	1.550 674 92	0.198 185 45	5.612 627 48
XLYP	1.0000	1.515 778 78	0.100 265 85	5.375 064 60

Table A6: BJ-damping parameter (DFT-D4(TB)-MBD) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
HF	1.0000	1.458 286 83	0.447 127 42	3.264 877 34
BLYP	1.0000	2.081 170 58	0.417 116 42	4.039 551 28
BPBE	1.0000	3.642 591 75	0.470 638 78	4.347 122 79
BP	1.0000	3.111 124 73	0.409 953 87	4.910 053 30
BPW	1.0000	2.527 447 27	0.404 027 82	4.220 840 57
LB94	1.0000	2.091 418 91	0.301 280 51	3.457 880 60
MPWLYP	1.0000	1.364 602 00	0.286 102 46	4.910 280 62
MPWPW	1.0000	1.731 307 52	0.325 479 73	4.813 726 63
OLYP	1.0000	2.301 876 44	0.541 547 21	2.532 872 78
OPBE	1.0000	2.478 622 43	0.598 057 92	2.266 713 22
PBE	1.0000	0.951 596 05	0.404 363 18	4.650 108 56
RPBE	1.0000	1.054 014 23	0.425 996 48	3.101 463 07
REVPBE	1.0000	1.528 500 98	0.493 140 34	3.104 412 25
PW86PBE	1.0000	1.464 972 96	0.426 357 74	4.670 700 01
RPW86PBE	1.0000	1.237 829 81	0.397 853 99	4.694 122 60
PW91	1.0000	0.896 485 32	0.395 924 18	4.963 209 77
PWP	1.0000	0.638 069 44	0.473 907 87	5.665 152 08
XLYP	1.0000	1.509 940 82	0.090 512 15	5.362 052 96
B97	1.0000	0.897 997 38	0.308 190 88	4.443 242 65
TPSS	1.0000	1.889 016 38	0.427 750 15	4.553 799 80
REVTPSS	1.0000	1.508 830 62	0.430 175 30	4.657 836 11
SCAN	1.0000	0.469 902 09	0.614 364 50	5.899 114 95
B1LYP	1.0000	1.830 749 38	0.384 935 43	4.455 926 40
B3LYP	1.0000	1.936 427 73	0.404 453 81	4.457 046 39
BHLYP	1.0000	1.518 967 70	0.281 922 18	5.294 274 69
B1P	1.0000	3.416 751 21	0.482 535 11	5.033 893 54
B3P	1.0000	3.182 790 35	0.469 923 25	4.976 502 53
B3PW	1.0000	2.723 632 74	0.443 772 56	4.522 155 74
O3LYP	1.0000	1.738 749 42	0.106 389 82	6.049 817 36
REVPBE0	1.0000	1.498 907 14	0.358 195 41	4.159 479 55
REVPBE38	1.0000	1.573 825 08	0.378 387 02	4.356 324 32
PBE0	1.0000	1.196 619 78	0.417 343 08	4.884 320 30
PWP1	1.0000	0.648 889 26	0.555 648 09	5.322 126 39
PW1PW	1.0000	1.183 642 44	0.469 537 24	4.882 722 76
MPW1PW	1.0000	1.627 884 71	0.415 576 75	4.599 734 89
MPW1LYP	1.0000	1.331 709 09	0.298 309 06	5.173 450 35
PW6B95	1.0000	−0.164 439 19	0.079 049 89	5.944 396 46
TPSSH	1.0000	2.164 689 07	0.452 541 89	4.655 539 22
TPSS0	1.0000	1.252 851 63	0.382 234 99	4.615 935 29
X3LYP	1.0000	1.505 628 53	0.211 527 28	5.479 016 28
M06L	1.0000	0.013 476 97	0.708 346 64	6.033 155 16
M06	1.0000	0.507 850 08	0.589 531 57	5.973 170 57
M062X	1.0000	0.046 726 18	0.870 981 56	7.329 886 30
WB97	1.0000	1.127 363 63	0.753 965 90	7.310 529 61
WB97X	1.0000	0.350 405 01	0.569 747 96	6.443 277 94

Table A6: BJ-damping parameter (DFT-D4(TB)-MBD) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
CAMB3LYP	1.0000	1.652 134 37	0.426 762 06	4.994 505 82
LCBLYP	1.0000	1.674 590 38	0.647 725 66	7.026 910 22
LH07TSVWN	1.0000	1.647 164 68	0.360 275 50	3.948 840 94
LH07SSVWN	1.0000	2.547 734 75	0.371 967 19	3.898 640 94
LH12CTSSIRPW92	1.0000	1.900 238 51	0.335 135 81	3.537 246 35
LH12CTSSIFPW92	1.0000	2.043 716 41	0.332 387 88	3.472 347 11
LH14TCALPBE	1.0000	0.962 171 13	0.408 097 99	4.539 119 55
B2PLYP	0.7800	0.970 900 85	0.418 492 25	4.592 862 43
MPW2PLYP	0.7500	0.555 068 01	0.481 488 34	4.881 793 16
PWPB95	0.8200	−0.026 408 53	0.437 447 68	4.538 847 24
DSDBLYP	0.5400	0.626 421 44	0.455 895 98	4.730 622 94
DSDPBE	0.4500	0.692 291 05	0.415 844 08	4.528 969 60
DSDPBEB95	0.5400	−0.025 356 83	0.431 175 70	4.317 249 07
DSDPBEP86	0.4700	0.404 372 39	0.526 926 25	5.086 782 49
DSDSVWN	0.4100	0.736 685 21	0.505 412 52	5.060 789 30
DODBLYP	0.4700	1.043 849 62	0.370 017 61	4.220 416 49
DODPBE	0.4800	0.808 244 28	0.383 864 76	4.375 732 21
DODPBEB95	0.5600	0.027 816 76	0.381 004 06	4.187 292 80
DODPBEP86	0.4600	0.711 638 46	0.409 071 64	4.513 968 86
DODSVWN	0.4200	0.829 595 03	0.459 577 76	4.896 713 68
PBE0-2	0.5000	0.124 815 39	0.661 505 25	5.701 644 63
PBE0-DH	0.8750	0.656 747 32	0.471 311 18	4.828 169 82

Table A7: BJ-damping parameter (DFT-D4(TB)-ATM) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
HF	1.0000	1.557 366 44	0.442 179 52	3.324 104 41
BLYP	1.0000	2.190 200 80	0.429 130 71	4.051 104 79
BPBE	1.0000	3.629 749 20	0.471 793 11	4.348 327 82
BP	1.0000	3.086 472 46	0.411 621 12	4.919 543 19
BPW	1.0000	2.851 090 94	0.454 632 14	4.143 451 06
LB94	1.0000	2.398 093 64	0.363 471 55	3.341 953 90
MPWLYP	1.0000	1.363 957 83	0.286 024 41	4.910 545 88
MPWPW	1.0000	1.731 856 25	0.325 344 35	4.813 184 52
OLYP	1.0000	2.300 871 26	0.541 448 59	2.533 323 00
OPBE	1.0000	2.709 625 30	0.618 003 52	2.276 211 23
PBE	1.0000	0.936 250 94	0.407 900 49	4.651 359 44
RPBE	1.0000	1.051 644 27	0.425 926 27	3.100 371 33
REVPBE	1.0000	1.611 382 01	0.512 152 00	3.047 183 55
PW86PBE	1.0000	1.192 546 14	0.397 454 89	4.661 501 28
RPW86PBE	1.0000	1.222 892 66	0.399 460 65	4.702 314 15
PW91	1.0000	0.782 210 05	0.390 973 90	4.944 084 51
PWP	1.0000	0.612 188 26	0.477 789 63	5.646 056 64
XLYP	1.0000	1.509 681 43	0.090 563 06	5.362 239 75
B97	1.0000	0.898 180 05	0.308 912 58	4.443 795 03
TPSS	1.0000	2.223 366 84	0.449 039 31	4.650 805 32
REVTPSS	1.0000	1.493 740 36	0.431 991 83	4.664 057 59
SCAN	1.0000	0.457 756 48	0.616 693 42	5.905 234 68
B1LYP	1.0000	1.828 196 41	0.385 610 62	4.461 051 23
B3LYP	1.0000	1.930 777 74	0.405 207 81	4.462 552 49
BHLYP	1.0000	1.506 555 02	0.283 550 60	5.303 546 38
B1P	1.0000	3.394 006 23	0.483 891 19	5.039 821 46
B3P	1.0000	3.161 907 35	0.471 032 71	4.981 373 63
B3PW	1.0000	2.712 739 65	0.446 318 95	4.525 179 62
O3LYP	1.0000	1.723 211 98	0.108 025 98	6.061 266 61
REVPBE0	1.0000	1.500 463 46	0.358 374 24	4.159 799 87
REVPBE38	1.0000	1.619 949 00	0.384 562 95	4.374 873 40
PBE0	1.0000	1.184 973 26	0.419 185 88	4.891 700 85
PWP1	1.0000	0.613 686 82	0.556 828 03	5.332 668 14
PW1PW	1.0000	1.160 028 22	0.470 785 18	4.892 430 94
MPW1PW	1.0000	1.619 913 31	0.417 097 90	4.607 283 22
MPW1LYP	1.0000	1.325 394 33	0.301 234 36	5.175 749 56
PW6B95	1.0000	−0.243 642 76	0.068 613 69	5.893 703 10
TPSSH	1.0000	1.816 993 05	0.437 085 55	4.576 793 51
TPSS0	1.0000	1.469 388 02	0.397 514 11	4.710 147 42
X3LYP	1.0000	1.494 935 75	0.213 108 66	5.487 460 09
M06L	1.0000	0.025 399 65	0.711 107 72	6.050 635 04
M06	1.0000	0.502 957 55	0.588 756 42	5.965 574 87
M062X	1.0000	−0.127 702 86	0.862 899 08	7.307 616 22
WB97	1.0000	1.262 045 57	0.754 376 95	7.315 277 80
WB97X	1.0000	0.347 835 80	0.574 882 91	6.419 218 02

Table A7: BJ-damping parameter (DFT-D4(TB)-ATM) for various DFAs as derived by fitting to reference data (S66x8 [16], S22x5 [17], NCIBLIND10 [18]).

DFA	s_6	s_8	a_1	a_2
CAMB3LYP	1.0000	1.639 669 17	0.424 278 08	5.031 098 15
LCBLYP	1.0000	1.678 383 79	0.647 054 35	7.028 833 75
LH07TSVWN	1.0000	3.408 582 18	0.532 185 98	3.550 686 20
LH07SSVWN	1.0000	2.017 420 30	0.499 831 99	3.534 492 78
LH12CTSSIRPW92	1.0000	2.466 883 56	0.567 836 03	2.831 261 77
LH12CTSSIFPW92	1.0000	2.703 768 07	0.586 232 58	2.721 033 81
LH14TCALPBE	1.0000	1.238 272 87	0.435 375 37	4.639 386 35
B2PLYP	0.7800	1.004 685 53	0.427 371 83	4.626 241 58
MPW2PLYP	0.7500	0.543 180 70	0.484 727 56	4.896 743 42
PWPB95	0.8200	−0.353 421 55	0.372 780 86	4.035 800 81
DSDBLYP	0.5400	0.601 512 54	0.460 913 02	4.753 484 49
DSDPBE	0.4500	0.698 655 39	0.425 083 71	4.565 189 30
DSDPBEB95	0.5400	−0.050 974 31	0.429 670 19	4.323 989 58
DSDPBEP86	0.4700	0.382 717 06	0.533 973 08	5.116 871 01
DSDSVWN	0.4100	0.509 046 43	0.494 132 32	4.920 923 77
DODBLYP	0.4700	1.171 014 52	0.398 337 37	4.258 098 11
DODPBE	0.4800	0.807 612 67	0.388 737 38	4.401 711 91
DODPBEB95	0.5600	0.009 590 16	0.388 667 13	4.094 626 93
DODPBEP86	0.4600	0.713 279 51	0.416 313 67	4.538 519 73
DODSVWN	0.4200	0.621 862 46	0.455 900 32	4.742 986 02
PBE0-2	0.5000	0.107 400 34	0.667 068 19	5.739 361 18
PBE0-DH	0.8750	0.748 647 13	0.475 982 57	4.909 100 90

F. Timings of energy and gradient calls

We compare timings for energy and gradient calls between DFT–D4 and DFT–D3(BJ)-ATM for the Tetrakis(isonitrile)rhodium(I) dimer with 106 atoms (doubly positively charged) and a diamond chunk with 430 atoms (286 carbon atoms and 144 hydrogen atoms) derived at four Intel(R) Core(TM) i7-6700 CPU (3.40 GHz).

Property	CPU time(DFT–D4) / s	CPU time(DFT–D3(BJ)-ATM) / s
Tetrakis(isonitrile)rhodium(I) dimer (106 atoms, charge +2)		
single–point	0.01	0.03
gradient	0.01	0.03
Diamond chunk (430 atoms, charge 0)		
single–point	0.34	0.41
gradient	0.51	1.02

Part II: Statistical measures and evaluations

G. Extendet statistical measures

As statistical measure for a set $\{\mathrm{x}_1,\ldots,\mathrm{x}_n\}$ of data points with references $\{\mathrm{r}_1,\ldots,\mathrm{r}_n\}$ we use

- Average : $\overline{x} = \frac{1}{n}\sum_i x_i$
- Mean deviation (MD): $MD = \frac{1}{n}\sum_i(\mathrm{x}_i - \mathrm{r}_i)$
- Mean absolute deviation (MAD): $MAD = \frac{1}{n}\sum_i |\mathrm{x}_i - \mathrm{r}_i|$
- Root mean square deviation (RMSD) : $\mathrm{RMSD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} x_i^2}$
- Bessel corrected variance (Var): $Var = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \overline{x})^2$
- Bessel corrected standard deviation (SD): $SD = \sqrt{\frac{1}{n-1}\sum_i(\mathrm{x}_i - \mathrm{r}_i - MD)^2}$
- Maximum deviation (Max): $Max = \max\{\mathrm{x}_i - \mathrm{r}_i\}$
- Minimum deviation (Min): $Min = \min\{\mathrm{x}_i - \mathrm{r}_i\}$
- Maximum absolute deviation (Amax): $Amax = \max\{|\mathrm{x}_i - \mathrm{r}_i|\}$

H. Statistical evaluation: S30L

Table A8: Extendet statistical evaluation of the S30L [19] benchmark set for various different DFAs. For each functional we directly compare DFT–D3 (BJ)-ATM (abbreviated as D3) corrected values with DFT–D4-ATM (abbreviated as D4) corrected values given in kcal mol^{-1}. For further details please check Ref. [20, 21]. We follow the numberation of the systems regarding Ref. [19]

	DLPNO-	PW6B95		SCAN		PBE	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
1	−31.0	−28.2	−30.1	−30.2	−29.7	−29.6	−28.0
2	−20.7	−19.0	−20.4	−19.8	−19.4	−19.6	−18.2
3	−23.3	−19.1	−19.2	−22.5	−21.5	−20.8	−18.0
4	−18.6	−20.9	−20.3	−21.4	−21.0	−20.7	−18.6
5	−27.9	−31.6	−32.9	−33.2	−32.2	−32.7	−28.7
6	−25.2	−21.2	−22.8	−25.6	−25.2	−24.8	−22.2
7	−31.0	−32.1	−33.4	−33.2	−33.2	−34.8	−29.9
8	−35.6	−36.9	−38.7	−38.1	−38.0	−40.2	−34.5
9	−33.7	−31.6	−32.7	−33.6	−29.4	−35.1	−27.0
10	−35.0	−30.5	−32.0	−34.7	−30.2	−36.2	−27.8
11	−35.8	−32.8	−36.7	−40.1	−34.2	−42.5	−32.5
12	−36.9	−33.6	−37.5	−40.1	−34.1	−42.5	−32.4
13	−27.3	−24.2	−25.7	−27.1	−25.5	−24.0	−22.9
14	−28.6	−24.2	−26.7	−28.3	−26.6	−25.6	−23.9
15	−17.5	−17.3	−18.1	−21.8	−21.9	−21.2	−21.1
16	−21.6	−21.4	−23.9	−24.2	−24.2	−25.3	−24.7
17	−34.3	−32.6	−31.7	−36.0	−35.9	−33.4	−32.3
18	−22.8	−20.8	−20.4	−24.4	−24.0	−22.5	−21.3
19	−15.3	−14.4	−14.7	−17.0	−16.1	−15.4	−15.3
20	−18.5	−17.2	−17.9	−20.1	−19.1	−18.0	−18.2
21	−28.0	−22.8	−24.9	−27.3	−25.1	−23.9	−23.5
22	−35.3	−35.2	−33.9	−38.6	−38.8	−39.5	−38.7
23	−62.1	−63.0	−61.8	−66.5	−66.9	−68.7	−68.1
24	−136.3	−130.3	−133.1	−138.0	−134.7	−126.9	−126.5
25	−28.7	−27.4	−31.2	−30.2	−28.9	−29.8	−27.1
26	−28.6	−26.4	−30.3	−27.9	−26.5	−29.8	−27.1
27	−83.4	−80.6	−82.0	−84.3	−83.5	−80.6	−80.7
28	−80.0	−77.4	−78.7	−80.7	−80.1	−77.2	−77.4
29	−52.8	−56.0	−54.2	−58.1	−58.2	−55.8	−54.2
30	−49.6	−51.1	−49.9	−53.6	−53.4	−51.5	−49.7
MD		1.5	0.3	−1.7	−0.4	−0.8	1.8
MAD		2.5	1.8	2.0	2.3	2.9	3.1
RMSD		2.9	2.2	2.6	2.7	3.6	3.8
SD		13.3	11.7	10.5	14.8	19.5	18.4
Var		6.1	4.7	3.8	7.6	13.1	11.7
Max		6.0	4.1	0.9	4.8	9.4	9.8
Min		−3.7	−5.0	−5.3	−5.4	−6.7	−6.0
AMax		6.0	5.0	5.3	5.4	9.4	9.8

Table A9: Extendet statistical evaluation of the S30L [19] benchmark set for various different DFAs. For each functional we directly compare DFT–D3 (BJ)-ATM (abbreviated as D3) corrected values with DFT–D4-MBD (abbreviated as D4) corrected values given in kcal mol^{-1}. For further details please check Ref. [20, 21]. We follow the numberation of the systems regarding Ref. [19]

	DLPNO-	PW6B95		SCAN		PBE	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
1	−31.0	−29.8	−30.1	−30.1	−29.7	−30.2	−28.0
2	−20.7	−20.2	−20.4	−19.7	−19.4	−20.0	−18.2
3	−23.3	−20.8	−19.2	−22.6	−21.5	−21.8	−18.0
4	−18.6	−21.5	−20.3	−21.5	−21.0	−21.1	−18.6
5	−27.9	−33.4	−32.9	−33.2	−32.2	−33.4	−28.7
6	−25.2	−22.9	−22.8	−25.6	−25.2	−25.5	−22.2
7	−31.0	−33.2	−33.4	−33.3	−33.2	−35.2	−29.9
8	−35.6	−38.2	−38.7	−38.1	−38.0	−40.5	−34.5
9	−33.7	−35.2	−32.7	−34.1	−29.4	−37.3	−27.0
10	−35.0	−34.6	−32.0	−35.3	−30.2	−38.6	−27.8
11	−35.8	−38.7	−36.7	−40.9	−34.2	−46.0	−32.5
12	−36.9	−39.4	−37.5	−40.9	−34.1	−45.9	−32.4
13	−27.3	−26.4	−25.7	−27.0	−25.5	−25.3	−22.9
14	−28.6	−26.8	−26.7	−28.2	−26.6	−27.0	−23.9
15	−17.5	−17.9	−18.1	−21.9	−21.9	−21.6	−21.1
16	−21.6	−22.4	−23.9	−24.3	−24.2	−25.9	−24.7
17	−34.3	−33.3	−31.7	−36.0	−35.9	−33.9	−32.3
18	−22.8	−21.6	−20.4	−24.4	−24.0	−23.1	−21.3
19	−15.3	−15.6	−14.7	−17.1	−16.1	−16.3	−15.3
20	−18.5	−19.0	−17.9	−20.2	−19.1	−19.3	−18.2
21	−28.0	−25.9	−24.9	−27.3	−25.1	−25.9	−23.5
22	−35.3	−35.5	−33.9	−38.7	−38.8	−39.8	−38.7
23	−62.1	−63.0	−61.8	−66.6	−66.9	−68.8	−68.1
24	−136.3	−135.9	−133.1	−138.5	−134.7	−130.8	−126.5
25	−28.7	−30.4	−31.2	−30.2	−28.9	−31.0	−27.1
26	−28.6	−29.5	−30.3	−27.8	−26.5	−31.0	−27.1
27	−83.4	−82.8	−82.0	−84.3	−83.5	−81.9	−80.7
28	−80.0	−79.1	−78.7	−80.6	−80.1	−78.2	−77.4
29	−52.8	−55.9	−54.2	−58.1	−58.2	−55.8	−54.2
30	−49.6	−51.3	−49.9	−53.6	−53.4	−51.6	−49.7
MD		−0.5	0.3	−1.8	−0.4	−1.9	1.8
MAD		1.5	1.8	2.1	2.3	3.1	3.1
RMSD		1.9	2.2	2.7	2.7	3.9	3.8
SD		10.2	11.7	10.8	14.8	18.8	18.4
Var		3.6	4.7	4.0	7.6	12.2	11.7
Max		2.5	4.1	1.0	4.8	5.5	9.8
Min		−5.5	−5.0	−5.3	−5.4	−10.2	−6.0
AMax		5.5	5.0	5.3	5.4	10.2	9.8

Table A10: Extendet statistical evaluation of the S30L [19] benchmark set for various different DFAs. For each functional we directly compare DFT–D3 (BJ)-ATM (abbreviated as D3) corrected values with DFT–D4(TB)-ATM (abbreviated as D4) corrected values given in kcal mol^{-1}. For further details please check Ref. [20, 21]. We follow the numberation of the systems regarding Ref. [19]

	DLPNO-	PW6B95		SCAN		PBE	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
1	−31.0	−29.0	−30.1	−29.5	−29.7	−29.6	−28.0
2	−20.7	−19.5	−20.4	−19.3	−19.4	−19.4	−18.2
3	−23.3	−19.5	−19.2	−21.9	−21.5	−20.6	−18.0
4	−18.6	−20.9	−20.3	−21.1	−21.0	−20.5	−18.6
5	−27.9	−32.1	−32.9	−32.4	−32.2	−31.9	−28.7
6	−25.2	−21.5	−22.8	−24.9	−25.2	−24.0	−22.2
7	−31.0	−32.5	−33.4	−32.3	−33.2	−33.8	−29.9
8	−35.6	−37.4	−38.7	−37.0	−38.0	−38.9	−34.5
9	−33.7	−31.7	−32.7	−31.3	−29.4	−33.2	−27.0
10	−35.0	−30.8	−32.0	−32.3	−30.2	−34.2	−27.8
11	−35.8	−33.3	−36.7	−37.0	−34.2	−40.1	−32.5
12	−36.9	−34.2	−37.5	−36.9	−34.1	−40.1	−32.4
13	−27.3	−25.5	−25.7	−26.7	−25.5	−24.8	−22.9
14	−28.6	−25.4	−26.7	−27.6	−26.6	−26.0	−23.9
15	−17.5	−17.6	−18.1	−21.5	−21.9	−21.1	−21.1
16	−21.6	−22.0	−23.9	−23.8	−24.2	−25.0	−24.7
17	−34.3	−32.3	−31.7	−35.5	−35.9	−32.9	−32.3
18	−22.8	−20.6	−20.4	−23.8	−24.0	−22.1	−21.3
19	−15.3	−14.8	−14.7	−16.6	−16.1	−15.7	−15.3
20	−18.5	−18.0	−17.9	−19.6	−19.1	−18.7	−18.2
21	−28.0	−25.4	−24.9	−27.1	−25.1	−26.6	−23.5
22	−35.3	−35.0	−33.9	−38.3	−38.8	−39.4	−38.7
23	−62.1	−62.5	−61.8	−66.3	−66.9	−68.4	−68.1
24	−136.3	−132.4	−133.1	−136.7	−134.7	−128.6	−126.5
25	−28.7	−28.3	−31.2	−29.2	−28.9	−29.1	−27.1
26	−28.6	−27.3	−30.3	−26.8	−26.5	−29.0	−27.1
27	−83.4	−81.5	−82.0	−84.1	−83.5	−81.2	−80.7
28	−80.0	−78.0	−78.7	−80.4	−80.1	−77.5	−77.4
29	−52.8	−56.2	−54.2	−58.3	−58.2	−56.3	−54.2
30	−49.6	−51.4	−49.9	−53.5	−53.4	−52.0	−49.7
MD		1.0	0.3	−0.9	−0.4	−0.5	1.8
MAD		2.0	1.8	1.8	2.3	2.4	3.1
RMSD		2.4	2.2	2.3	2.7	3.0	3.8
SD		11.8	11.7	11.5	14.8	16.1	18.4
Var		4.8	4.7	4.6	7.6	9.0	11.7
Max		4.2	4.1	2.7	4.8	7.7	9.8
Min		−4.2	−5.0	−5.5	−5.4	−6.3	−6.0
AMax		4.2	5.0	5.5	5.4	7.7	9.8

I. Statistical evaluation: L7

Table A11: Extended statistical evaluations of different DFAs with respect to DLPNO-CCSD(T)/CBS* data. For each functional we directly compare DFT–D3(BJ)-ATM (abbreviated as D3) corrected values with DFT–D4-ATM (abbreviated as D4) corrected values given in kcal mol^{-1}. We follow the numberation of the systems regarding Ref. [22].

	DLPNO-	PW6B95		PBE0		TPSS	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
CBH	−11.6	−8.2	−9.0	−10.8	−11.7	−10.8	−11.6
C2C2PD	−21.3	−18.8	−20.4	−20.1	−18.3	−23.9	−20.1
C3A	−17.0	−14.7	−14.9	−16.0	−14.4	−18.4	−15.3
C3GC	−29.1	−26.2	−26.6	−27.0	−24.2	−31.1	−25.9
GCGC	−12.8	−13.5	−12.4	−14.1	−12.1	−15.8	−12.5
GGG	−1.9	−1.8	−1.4	−2.1	−1.3	−3.0	−1.6
PHE	−23.0	−23.7	−23.7	−25.4	−25.3	−24.2	−23.9
MD		1.4	1.2	0.2	1.3	−1.5	0.8
MAD		1.8	1.4	1.3	2.0	1.7	1.1
RMSD		2.2	1.7	1.5	2.6	1.9	1.5
SD		4.3	3.1	3.9	5.8	3.1	3.3
Var		3.1	1.6	2.5	5.7	1.6	1.8
Max		3.4	2.6	2.1	4.9	0.8	3.2
Min		−0.7	−0.7	−2.4	−2.3	−3.0	−0.9
AMax		3.4	2.6	2.4	4.9	3.0	3.2

Table A12: Extended statistical evaluations of different DFAs with respect to DLPNO-CCSD(T)/CBS* data. For each functional we directly compare DFT–D3 (BJ)-ATM (abbreviated as D3) corrected values with DFT–D4-MBD (abbreviated as D4) corrected values given in kcal mol^{-1}. We follow the numberation of the systems regarding Ref. [22].

	DLPNO-	PW6B95		PBE0		TPSS	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
CBH	−11.6	−8.6	−9.0	−11.0	−11.7	−10.8	−11.6
C2C2PD	−21.3	−20.5	−20.4	−20.3	−18.3	−23.6	−20.1
C3A	−17.0	−15.6	−14.9	−16.1	−14.4	−18.1	−15.3
C3GC	−29.1	−27.8	−26.6	−27.2	−24.2	−30.7	−25.9
GCGC	−12.8	−13.9	−12.4	−14.1	−12.1	−15.6	−12.5
GGG	−1.9	−2.0	−1.4	−2.1	−1.3	−2.8	−1.6
PHE	−23.0	−24.0	−23.7	−25.6	−25.3	−24.3	−23.9
MD		0.6	1.2	0.1	1.3	−1.3	0.8
MAD		1.2	1.4	1.2	2.0	1.5	1.1
RMSD		1.5	1.7	1.4	2.6	1.7	1.5
SD		3.6	3.1	3.7	5.8	2.8	3.3
Var		2.1	1.6	2.3	5.7	1.3	1.8
Max		3.0	2.6	1.9	4.9	0.8	3.2
Min		−1.1	−0.7	−2.6	−2.3	−2.8	−0.9
AMax		3.0	2.6	2.6	4.9	2.8	3.2

Table A13: Extended statistical evaluations of different DFAs with respect to DLPNO-CCSD(T)/CBS* data. For each functional we directly compare DFT–D3 (BJ)-ATM (abbreviated as D3) corrected values with DFT–D4(TB)-ATM (abbreviated as D4) corrected values given in kcal mol^{-1}. We follow the numberation of the systems regarding Ref. [22].

	DLPNO-	PW6B95		PBE0		TPSS	
#	CCSD(T)/CBS*	D4	D3	D4	D3	D4	D3
CBH	−11.6	−9.0	−9.0	−11.8	−11.7	−12.1	−11.6
C2C2PD	−21.3	−18.7	−20.4	−20.0	−18.3	−23.7	−20.1
C3A	−17.0	−14.6	−14.9	−16.0	−14.4	−18.3	−15.3
C3GC	−29.1	−26.2	−26.6	−26.9	−24.2	−31.0	−25.9
GCGC	−12.8	−13.4	−12.4	−14.1	−12.1	−15.7	−12.5
GGG	−1.9	−1.8	−1.4	−2.2	−1.3	−3.0	−1.6
PHE	−23.0	−23.8	−23.7	−25.6	−25.3	−24.4	−23.9
MD		1.3	1.2	0.0	1.3	−1.7	0.8
MAD		1.7	1.4	1.2	2.0	1.7	1.1
RMSD		2.0	1.7	1.5	2.6	1.8	1.5
SD		4.1	3.1	4.0	5.8	2.0	3.3
Var		2.8	1.6	2.6	5.7	0.7	1.8
Max		2.9	2.6	2.2	4.9	−0.5	3.2
Min		−0.8	−0.7	−2.6	−2.3	−2.9	−0.9
AMax		2.9	2.6	2.6	4.9	2.9	3.2

J. Statistical evaluation: MOR41

We follow the numberation of the systems regarding Ref. [23].

Table A14: Extendet statistical evaluations of : DOD-PBE and DSD-PBE in kcal mol^{-1}. We abbreviate D3(BJ)-ATM by D3.

		DOD-PBE			DSD-PBE		
#	Ref.	D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	−43.1	−46.2	−46.3	−46.4	−48.4	−48.5	−49.7
2	−46.6	−51.6	−51.8	−51.9	−54.2	−54.3	−55.4
3	−27.6	−35.8	−36.0	−36.0	−39.4	−39.4	−40.3
4	−62.5	−60.3	−60.5	−60.6	−58.5	−58.6	−59.4
5	3.7	2.9	2.7	2.6	3.7	3.6	3.0
6	−23.1	−21.7	−21.7	−21.8	−22.9	−22.9	−21.9
7	−16.2	−14.3	−14.2	−14.5	−14.8	−14.8	−13.3
8	−17.2	−13.5	−13.7	−14.0	−13.2	−13.3	−13.3
9	−18.8	−14.5	−14.6	−15.0	−14.2	−14.3	−13.2
10	−22.6	−21.9	−22.1	−22.1	−23.3	−23.4	−24.6
11	27.0	24.7	24.7	24.5	23.0	23.0	21.4
12	−29.8	−33.4	−33.5	−33.6	−35.5	−35.6	−35.2
13	−43.2	−45.8	−46.0	−46.0	−47.7	−47.8	−49.2
14	−52.0	−53.7	−54.0	−54.5	−55.1	−55.4	−56.7
15	−4.1	7.5	7.3	7.3	11.8	11.6	12.1
16	−39.8	−40.3	−40.8	−41.1	−40.3	−40.8	−41.7
17	−16.1	−13.9	−14.0	−14.0	−14.0	−14.1	−11.8
18	−34.2	−34.0	−34.4	−34.8	−33.7	−33.9	−36.2
19	−40.1	−39.9	−40.3	−40.7	−39.4	−39.6	−41.9
20	−30.2	−29.5	−29.8	−30.1	−28.8	−28.9	−30.9
21	−15.1	−17.2	−17.7	−18.1	−15.8	−16.1	−17.3
22	−35.9	−39.0	−39.4	−39.9	−40.3	−40.6	−42.6
23	−55.0	−55.1	−55.6	−56.1	−54.8	−55.1	−57.9
24	−41.6	−40.2	−41.1	−41.4	−39.9	−40.7	−42.7
25	−45.9	−45.2	−46.3	−46.4	−45.4	−46.3	−48.1
26	−36.4	−34.9	−35.2	−35.3	−33.3	−33.5	−34.7
27	−21.8	−21.1	−21.2	−21.3	−19.8	−19.9	−21.0
28	−36.3	−35.9	−36.1	−36.2	−34.6	−34.7	−36.0
29	−28.3	−28.7	−28.9	−28.8	−27.9	−28.0	−29.2
30	−14.9	−16.0	−16.2	−16.1	−14.9	−15.1	−15.8
31	−29.9	−29.4	−29.8	−30.1	−28.6	−28.9	−30.1
32	−1.9	−2.0	−2.0	−1.9	−2.3	−2.2	−2.1
33	−10.7	−6.7	−6.7	−6.7	−4.2	−4.2	−2.8
34	−25.6	−22.9	−23.0	−23.1	−21.0	−21.1	−21.3
35	−30.9	−28.3	−28.4	−28.7	−26.6	−26.7	−27.4
36	−39.8	−40.2	−40.4	−40.7	−40.0	−40.0	−41.1
37	−14.0	−16.9	−17.4	−17.3	−16.0	−16.4	−16.6
38	−64.4	−68.1	−68.6	−69.0	−67.4	−67.9	−74.0
39	−63.9	−63.3	−63.9	−64.5	−63.7	−64.0	−66.3
40	−65.8	−65.2	−65.4	−65.5	−64.9	−65.0	−67.7
41	−3.2	−2.4	−2.3	−2.4	−2.1	−2.1	−0.7
MD		0.1	−0.2	−0.3	0.2	0.0	−0.9
MAD		2.1	2.1	2.2	2.9	2.9	3.7
RMSD		3.1	3.1	3.1	4.3	4.3	5.0
SD		19.7	19.9	20.0	27.5	27.6	31.8
Var		9.7	9.9	10.0	18.9	19.0	25.3
Max		11.5	11.4	11.4	15.8	15.7	16.2
Min		−8.2	−8.4	−8.4	−11.8	−11.9	−12.7
AMax		11.5	11.4	11.4	15.8	15.7	16.2

Table A15: Extendet statistical evaluations of : B3LYP and PBE0 in kcal mol^{-1}. We abbreviate D3(BJ)-ATM by D3.

		B3LYP			PBE0		
#	Ref.	D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	−43.1	−40.5	−40.6	−40.7	−44.6	−44.6	−44.7
2	−46.6	−41.9	−42.0	−42.0	−47.4	−47.4	−47.4
3	−27.6	−22.8	−22.9	−22.8	−26.4	−26.5	−26.4
4	−62.5	−66.2	−66.4	−66.5	−71.3	−71.4	−71.4
5	3.7	−0.1	−0.1	−0.2	−2.6	−2.7	−2.4
6	−23.1	−17.4	−17.4	−17.5	−21.0	−21.0	−20.3
7	−16.2	−12.1	−12.0	−12.8	−15.7	−15.6	−15.3
8	−17.2	−12.8	−12.9	−13.3	−16.0	−16.0	−15.3
9	−18.8	−14.3	−14.3	−15.1	−16.1	−16.1	−15.0
10	−22.6	−16.4	−16.6	−16.4	−19.4	−19.4	−19.1
11	27.0	30.0	30.1	29.8	30.9	30.9	30.2
12	−29.8	−24.6	−24.6	−24.7	−29.9	−29.9	−28.9
13	−43.2	−38.0	−38.1	−37.9	−43.9	−43.9	−43.6
14	−52.0	−43.8	−44.0	−44.7	−50.9	−51.1	−50.5
15	−4.1	−5.0	−5.1	−5.1	−4.8	−4.9	−4.4
16	−39.8	−39.3	−39.8	−39.9	−40.4	−40.7	−40.0
17	−16.1	−14.5	−14.6	−14.5	−13.7	−13.7	−11.2
18	−34.2	−31.8	−32.0	−31.9	−33.3	−33.4	−32.8
19	−40.1	−37.2	−37.4	−37.3	−38.7	−38.7	−38.0
20	−30.2	−29.2	−29.4	−29.3	−28.6	−28.6	−27.8
21	−15.1	−18.5	−18.8	−19.0	−18.7	−18.8	−17.1
22	−35.9	−32.3	−32.6	−32.6	−33.5	−33.7	−32.1
23	−55.0	−51.2	−51.4	−51.3	−52.6	−52.8	−52.3
24	−41.6	−40.8	−41.7	−41.5	−41.3	−42.0	−41.7
25	−45.9	−45.4	−46.4	−46.0	−45.6	−46.4	−45.6
26	−36.4	−42.4	−42.6	−42.5	−38.5	−38.7	−39.0
27	−21.8	−26.8	−27.0	−27.1	−25.1	−25.3	−25.5
28	−36.3	−41.7	−41.9	−41.8	−39.2	−39.4	−39.5
29	−28.3	−32.8	−33.0	−32.6	−30.0	−30.1	−30.0
30	−14.9	−21.8	−22.1	−21.6	−16.3	−16.6	−16.1
31	−29.9	−32.8	−33.2	−33.5	−29.4	−29.8	−29.7
32	−1.9	0.1	0.1	0.5	0.2	0.2	0.7
33	−10.7	−18.9	−19.0	−19.1	−9.4	−9.5	−8.8
34	−25.6	−30.3	−30.5	−30.6	−25.1	−25.2	−25.0
35	−30.9	−34.6	−34.7	−34.9	−29.8	−29.9	−29.9
36	−39.8	−39.4	−39.5	−39.7	−34.9	−34.9	−35.3
37	−14.0	−33.0	−33.4	−33.4	−23.3	−23.5	−23.4
38	−64.4	−72.2	−72.6	−72.6	−69.1	−69.4	−71.8
39	−63.9	−58.2	−58.5	−59.0	−60.7	−60.9	−59.5
40	−65.8	−66.4	−66.5	−66.3	−69.0	−69.1	−69.2
41	−3.2	−6.3	−6.3	−6.6	−3.0	−3.0	−3.4
MD		−0.1	−0.3	−0.4	−0.3	−0.4	0.0
MAD		4.2	4.2	4.2	2.3	2.3	2.6
RMSD		5.3	5.3	5.2	3.1	3.1	3.4
SD		33.7	33.9	33.5	19.7	19.8	21.8
Var		28.3	28.8	28.0	9.7	9.8	11.9
Max		8.2	7.9	7.3	5.0	4.9	4.9
Min		−19.0	−19.4	−19.3	−9.2	−9.5	−9.4
AMax		19.0	19.4	19.3	9.2	9.5	9.4

Table A16: Extendet statistical evaluations of : PW6B95 and CAM-B3LYP in kcal mol^{-1}. We abbreviate D3(BJ)-ATM by D3.

		PW6B95			CAM-B3LYP		
#	Ref.	D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	−43.1	−41.8	−41.8	−41.8	−40.1	−40.1	−40.1
2	−46.6	−42.9	−43.0	−42.9	−42.7	−42.8	−42.7
3	−27.6	−22.6	−22.6	−22.5	−23.2	−23.2	−23.1
4	−62.5	−63.0	−63.0	−63.0	−64.4	−64.4	−64.2
5	3.7	1.0	1.1	1.1	2.7	2.7	3.0
6	−23.1	−19.8	−19.7	−19.7	−19.5	−19.4	−18.6
7	−16.2	−16.5	−16.0	−16.0	−14.1	−14.1	−13.4
8	−17.2	−12.2	−12.4	−12.6	−15.8	−15.8	−14.8
9	−18.8	−12.5	−12.3	−12.2	−17.8	−17.8	−16.5
10	−22.6	−15.5	−15.6	−15.6	−15.8	−15.9	−15.3
11	27.0	32.8	33.0	32.7	33.6	33.7	33.1
12	−29.8	−28.4	−28.2	−28.2	−24.3	−24.3	−23.0
13	−43.2	−40.9	−40.7	−40.7	−38.4	−38.4	−37.9
14	−52.0	−47.9	−48.1	−48.6	−44.1	−44.3	−43.5
15	−4.1	−3.9	−4.0	−3.8	−9.6	−9.7	−9.1
16	−39.8	−40.0	−40.5	−40.8	−39.0	−39.3	−38.2
17	−16.1	−15.2	−15.2	−15.0	−16.2	−16.3	−13.1
18	−34.2	−29.4	−29.3	−31.0	−30.2	−30.3	−29.8
19	−40.1	−34.5	−34.5	−36.2	−36.4	−36.5	−35.9
20	−30.2	−27.1	−26.9	−27.8	−28.2	−28.3	−27.3
21	−15.1	−16.0	−16.1	−17.5	−14.4	−14.6	−12.8
22	−35.9	−26.1	−26.6	−29.1	−27.4	−27.6	−26.5
23	−55.0	−46.8	−46.7	−49.2	−49.0	−49.1	−49.2
24	−41.6	−39.7	−41.2	−42.0	−40.7	−41.3	−41.0
25	−45.9	−43.0	−44.7	−45.4	−45.0	−45.6	−44.7
26	−36.4	−33.5	−34.2	−34.8	−42.1	−42.3	−42.9
27	−21.8	−21.4	−22.1	−22.7	−27.4	−27.5	−28.2
28	−36.3	−34.3	−34.9	−35.6	−41.8	−41.9	−42.6
29	−28.3	−26.1	−26.7	−27.0	−32.1	−32.2	−32.4
30	−14.9	−9.9	−10.6	−11.0	−17.4	−17.7	−17.7
31	−29.9	−25.4	−26.4	−26.8	−33.3	−33.6	−34.1
32	−1.9	−1.2	−1.1	−1.2	0.5	0.5	0.8
33	−10.7	−10.5	−10.7	−10.7	−18.5	−18.6	−18.1
34	−25.6	−24.1	−24.4	−24.9	−28.6	−28.7	−28.8
35	−30.9	−28.7	−29.0	−30.0	−32.7	−32.9	−33.3
36	−39.8	−33.5	−33.5	−35.2	−36.5	−36.6	−37.7
37	−14.0	−19.6	−20.2	−19.6	−26.7	−26.9	−26.9
38	−64.4	−59.6	−60.5	−61.7	−67.0	−67.3	−70.0
39	−63.9	−61.0	−61.2	−62.4	−60.8	−60.9	−59.8
40	−65.8	−66.2	−66.2	−66.8	−65.9	−66.0	−66.2
41	−3.2	−1.0	−1.4	−1.4	−5.9	−6.0	−6.6
MD		2.7	2.4	1.9	0.5	0.4	0.7
MAD		3.2	3.0	2.6	3.7	3.7	4.3
RMSD		4.0	3.8	3.3	4.6	4.6	5.0
SD		18.9	19.1	17.2	28.9	29.1	31.4
Var		8.9	9.1	7.4	21.0	21.2	24.7
Max		9.8	9.2	7.1	8.5	8.3	9.3
Min		−5.6	−6.2	−5.6	−12.7	−12.8	−12.8
AMax		9.8	9.2	7.1	12.7	12.8	12.8

Table A17: Extendet statistical evaluations of : revPBE and M06L in kcal mol^{-1}. We abbreviate D3(BJ)-ATM by D3.

		revPBE			M06L		
#	Ref.	D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	−43.1	−44.5	−44.6	−45.0	−41.0	−41.0	−40.7
2	−46.6	−47.6	−47.6	−48.0	−45.1	−45.1	−44.9
3	−27.6	−29.0	−29.1	−29.2	−27.1	−27.1	−26.9
4	−62.5	−73.6	−73.8	−74.5	−64.9	−64.9	−64.7
5	3.7	−6.8	−6.7	−7.1	−2.7	−2.7	−2.5
6	−23.1	−17.9	−17.9	−18.1	−18.1	−18.1	−18.1
7	−16.2	−12.9	−12.9	−13.3	−16.8	−16.8	−16.8
8	−17.2	−14.2	−14.3	−15.3	−7.7	−7.7	−7.5
9	−18.8	−14.0	−13.8	−15.0	−7.2	−7.2	−8.2
10	−22.6	−24.6	−24.7	−25.0	−13.2	−13.2	−12.7
11	27.0	24.2	24.5	23.9	30.7	30.7	31.3
12	−29.8	−30.6	−30.4	−30.9	−24.7	−24.7	−24.3
13	−43.2	−44.8	−44.7	−45.0	−39.8	−39.8	−39.4
14	−52.0	−51.2	−51.3	−52.9	−50.0	−50.0	−49.2
15	−4.1	1.9	1.7	1.6	5.4	5.4	5.5
16	−39.8	−41.7	−42.0	−43.0	−42.3	−42.3	−40.6
17	−16.1	−14.8	−14.9	−14.7	−18.2	−18.2	−17.7
18	−34.2	−34.8	−34.5	−35.7	−24.7	−24.7	−23.9
19	−40.1	−39.0	−38.5	−39.9	−28.8	−28.8	−27.7
20	−30.2	−31.2	−30.9	−31.9	−24.6	−24.6	−23.6
21	−15.1	−23.9	−23.7	−25.2	−13.7	−13.7	−12.7
22	−35.9	−37.5	−37.1	−38.5	−21.8	−21.7	−20.7
23	−55.0	−52.2	−51.6	−53.4	−40.8	−40.8	−39.8
24	−41.6	−39.1	−40.0	−41.0	−39.0	−38.9	−36.8
25	−45.9	−43.5	−44.7	−45.3	−44.0	−43.9	−41.1
26	−36.4	−35.5	−35.6	−36.1	−33.7	−33.7	−33.0
27	−21.8	−21.5	−21.7	−22.2	−22.2	−22.2	−22.1
28	−36.3	−36.0	−36.2	−36.6	−33.9	−33.9	−33.5
29	−28.3	−28.9	−29.1	−28.8	−25.7	−25.7	−25.4
30	−14.9	−23.2	−23.2	−22.9	−12.4	−12.4	−12.2
31	−29.9	−28.0	−28.4	−29.3	−23.8	−23.8	−23.9
32	−1.9	−0.5	−0.3	0.2	1.4	1.4	1.4
33	−10.7	−10.5	−10.6	−10.4	−12.1	−12.1	−11.8
34	−25.6	−25.1	−25.1	−25.5	−22.1	−22.1	−21.7
35	−30.9	−29.1	−29.0	−29.8	−23.6	−23.5	−23.2
36	−39.8	−33.6	−33.2	−34.5	−29.8	−29.8	−29.6
37	−14.0	−29.7	−30.4	−30.5	−26.4	−26.5	−26.1
38	−64.4	−73.0	−73.0	−74.4	−59.1	−59.1	−57.4
39	−63.9	−56.7	−56.8	−59.0	−56.1	−56.1	−55.6
40	−65.8	−66.7	−66.5	−66.9	−65.0	−65.0	−64.7
41	−3.2	−1.3	−1.4	−1.4	−4.7	−4.7	−4.9
MD		−0.6	−0.6	−1.3	3.6	3.6	4.2
MAD		3.3	3.3	3.2	5.1	5.1	5.4
RMSD		4.8	4.9	4.9	6.4	6.4	6.8
SD		30.7	31.0	30.5	34.1	34.1	34.5
Var		23.6	24.1	23.3	29.1	29.1	29.7
Max		7.2	7.2	5.7	14.2	14.2	15.2
Min		−15.7	−16.3	−16.5	−12.4	−12.5	−12.1
AMax		15.7	16.3	16.5	14.2	14.2	15.2

Table A18: Extendet statistical evaluations of : PBE and RPBE in kcal mol^{-1}. We abbreviate D3(BJ)-ATM by D3.

		PBE			RPBE		
#	Ref.	D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	−43.1	−46.7	−46.8	−46.7	−44.4	−44.6	−49.0
2	−46.6	−50.0	−50.0	−50.0	−47.3	−47.6	−51.6
3	−27.6	−31.5	−31.5	−31.4	−28.8	−29.0	−31.8
4	−62.5	−75.1	−75.2	−75.2	−74.0	−74.5	−76.4
5	3.7	−7.4	−7.4	−7.4	−7.2	−7.2	−8.6
6	−23.1	−20.4	−20.4	−20.4	−17.7	−17.8	−11.6
7	−16.2	−14.9	−14.8	−15.3	−12.1	−11.7	−4.3
8	−17.2	−14.4	−14.5	−14.7	−14.1	−14.4	−13.6
9	−18.8	−16.0	−15.9	−16.4	−15.3	−15.2	−10.5
10	−22.6	−24.5	−24.6	−24.4	−24.6	−24.9	−28.1
11	27.0	25.0	25.0	25.0	24.4	24.9	18.2
12	−29.8	−30.8	−30.7	−30.6	−30.8	−30.8	−26.0
13	−43.2	−45.2	−45.2	−45.0	−44.9	−45.1	−48.9
14	−52.0	−52.3	−52.5	−52.6	−51.2	−51.5	−55.5
15	−4.1	1.2	1.1	1.1	1.2	0.8	3.8
16	−39.8	−39.5	−39.9	−39.7	−40.5	−41.0	−42.2
17	−16.1	−14.4	−14.5	−14.4	−14.6	−14.6	−2.1
18	−34.2	−32.5	−32.6	−32.1	−36.0	−36.0	−44.7
19	−40.1	−36.3	−36.4	−35.8	−39.9	−39.9	−48.6
20	−30.2	−28.1	−28.1	−27.7	−32.2	−32.1	−38.0
21	−15.1	−20.4	−20.6	−20.3	−25.2	−25.3	−28.0
22	−35.9	−35.2	−35.4	−34.7	−38.5	−38.6	−48.8
23	−55.0	−50.2	−50.3	−49.6	−53.8	−53.6	−65.6
24	−41.6	−36.8	−37.6	−37.2	−38.1	−39.4	−47.5
25	−45.9	−41.4	−42.3	−41.7	−41.6	−43.3	−50.6
26	−36.4	−34.9	−35.1	−34.9	−35.6	−35.9	−41.8
27	−21.8	−21.9	−22.1	−22.1	−21.8	−22.3	−30.1
28	−36.3	−35.5	−35.7	−35.5	−36.3	−36.8	−44.2
29	−28.3	−27.7	−27.8	−27.5	−29.0	−29.4	−35.5
30	−14.9	−19.9	−20.1	−19.7	−23.6	−23.8	−28.7
31	−29.9	−26.6	−26.9	−27.0	−28.9	−29.6	−36.5
32	−1.9	0.9	0.9	1.2	−0.5	−0.4	−0.4
33	−10.7	−9.5	−9.6	−9.7	−10.1	−10.1	−5.2
34	−25.6	−23.8	−23.9	−23.8	−25.0	−25.0	−27.0
35	−30.9	−28.1	−28.2	−28.1	−29.2	−29.2	−34.1
36	−39.8	−32.8	−32.9	−32.7	−34.3	−34.0	−41.5
37	−14.0	−29.8	−30.0	−30.0	−30.3	−31.3	−31.1
38	−64.4	−68.5	−68.8	−68.4	−73.9	−74.3	−99.4
39	−63.9	−57.0	−57.2	−57.1	−58.6	−59.5	−68.8
40	−65.8	−68.4	−68.5	−68.2	−67.4	−67.5	−79.4
41	−3.2	−2.8	−2.9	−3.2	−1.1	−1.0	2.6
MD		−0.1	−0.3	−0.1	−0.9	−1.1	−4.7
MAD		3.5	3.4	3.5	3.4	3.4	8.3
RMSD		4.8	4.7	4.8	5.0	5.1	10.1
SD		30.5	30.4	30.6	31.4	31.7	57.5
Var		23.3	23.0	23.4	24.6	25.2	82.6
Max		7.0	6.9	7.1	5.5	5.9	14.0
Min		−15.7	−16.0	−16.0	−16.2	−17.3	−35.0
AMax		15.7	16.0	16.0	16.2	17.3	35.0

K. Statistical evaluation: SCONF

Table A19: Reference values are calculated on a DLPNO-CCSD(T)/TightPNO/CBS(aug-cc-pVTZ/aug-cc-pVQZ) level of theory. We follow the nomenclature of the GMTKN55 [24] database. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		DSDBLYP		B3LYP		PW6B95		PBE	
#	Ref.	D4	D3	D4	D3	D4	D3	D4	D3
				ANGOL15					
C1–C2	0.9	0.9	0.9	0.8	0.8	0.9	0.9	0.8	0.8
C1–C3	2.3	2.2	2.2	2.5	2.6	2.5	2.5	3.2	3.2
C1–C4	3.1	3.1	3.1	3.2	3.3	3.3	3.3	3.9	3.9
C1–C5	4.6	4.5	4.5	4.5	4.4	4.7	4.7	5.1	5.1
C1–C6	4.9	4.8	4.8	4.7	4.7	5.1	5.1	5.4	5.4
C1–C7	4.2	4.2	4.2	4.6	4.5	4.3	4.2	5.3	5.3
C1–C8	4.4	4.3	4.3	4.7	4.5	4.4	4.3	5.3	5.2
C1–C9	6.2	6.2	6.1	6.2	6.0	6.4	6.3	6.8	6.6
C1–C10	6.2	6.1	6.1	6.3	6.1	6.5	6.4	7.1	6.9
C1–C11	5.7	5.6	5.6	5.9	5.7	5.8	5.7	6.5	6.4
C1–C12	5.6	5.6	5.6	6.0	5.8	5.8	5.7	6.7	6.6
C1–C13	5.9	5.8	5.8	6.0	5.7	6.7	6.5	6.8	6.7
C1–C14	6.3	6.3	6.3	6.4	6.2	6.5	6.4	6.8	6.7
C1–C15	6.2	6.3	6.2	6.5	6.0	6.2	6.0	6.8	6.5
				GLC4					
G1–G2	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2
G1–G3	6.2	6.2	6.3	5.3	5.6	4.8	5.0	4.6	4.8
G1–G4	5.5	5.1	5.2	3.5	3.8	4.8	5.0	2.6	2.8
MD		0.0	0.0	−0.1	−0.1	0.0	0.0	0.3	0.3
MAD		0.1	0.1	0.3	0.3	0.3	0.2	0.9	0.8
RMSD		0.1	0.1	0.6	0.5	0.4	0.4	1.1	1.0
SD		0.5	0.4	2.4	1.9	1.8	1.6	4.3	3.9
Var		0.0	0.0	0.3	0.2	0.2	0.2	1.1	0.9
Max		0.1	0.1	0.4	0.3	0.7	0.6	1.2	1.1
Min		−0.4	−0.4	−2.1	−1.7	−1.3	−1.2	−3.0	−2.7
AMax		0.4	0.4	2.1	1.7	1.3	1.2	3.0	2.7

L. Statistical evaluation: PCONF21

Table A20: The reference energies were generated on the DLPNO-CCSD(T)/TightPNO/CBS(aug-cc-pVTZ/aug-cc-pVQZ) level of theory while the original geometries were kept. We follow the nomenclature of the GMTKN55 [24] database. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		DSDBLYP		B3LYP		PW6B95		PBE	
#	Ref.	D4	D3	D4	D3	D4	D3	D4	D3
Tripeptides									
99–444	0.0	0.2	0.1	−0.3	−0.7	0.9	0.7	−2.2	−2.5
99–357	1.0	1.0	0.8	0.9	0.1	0.9	0.6	−1.0	−1.5
99–366	0.7	1.1	1.0	1.2	1.1	1.7	1.7	0.6	0.5
99–215	0.8	1.1	0.9	0.6	0.2	1.6	1.4	−1.2	−1.4
99–300	0.8	1.3	1.2	1.5	1.2	1.6	1.5	0.8	0.6
99–114	1.9	1.8	1.6	1.7	1.1	1.6	1.3	0.1	−0.3
99–412	2.2	2.2	2.1	2.0	1.9	2.1	2.1	1.4	1.4
99–691	1.6	1.9	1.8	1.9	1.8	2.3	2.3	1.1	1.1
99–470	1.9	2.0	1.9	2.3	1.7	2.6	2.3	1.4	1.0
99–224	2.1	1.8	1.7	1.2	1.0	2.9	2.8	−0.2	−0.4
GLY									
GLY_ab–GLY_aR	1.1	1.1	1.2	0.9	1.3	1.2	1.4	1.3	1.6
GLY_ab–GLY_pII	1.2	1.5	1.5	1.8	1.9	2.2	2.3	2.3	2.4
GLY_ab–GLY_aL	2.4	2.5	2.7	2.4	3.0	2.2	2.5	2.8	3.2
GLY_ab–GLY_b	2.1	1.8	1.9	1.8	1.8	2.1	2.1	1.3	1.3
SER									
SER_ab–SER_aR	1.5	1.6	1.6	1.6	1.9	1.6	1.7	2.0	2.2
SER_ab–SER_pII	2.8	3.1	3.2	3.2	3.5	3.6	3.7	3.9	4.0
SER_ab–SER_aL	2.3	2.7	2.8	2.6	3.2	1.8	2.1	3.4	3.7
SER_ab–SER_b	2.7	2.5	2.6	2.5	2.5	2.9	2.9	2.3	2.3
MD		0.1	0.1	0.0	0.0	0.4	0.3	−0.5	−0.5
MAD		0.2	0.2	0.3	0.5	0.5	0.5	1.0	1.2
RMSD		0.3	0.3	0.4	0.6	0.6	0.6	1.2	1.4
SD		1.0	1.2	1.7	2.6	2.0	2.0	4.8	5.7
Var		0.1	0.1	0.2	0.4	0.2	0.2	1.4	1.9
Max		0.5	0.6	0.7	0.9	1.0	1.0	1.1	1.5
Min		−0.3	−0.4	−0.9	−1.1	−0.5	−0.6	−2.3	−2.5
AMax		0.5	0.6	0.9	1.1	1.0	1.0	2.3	2.5

M. Statistical evaluation: ICONF

Table A21: Reference energies are obtained with the W1–F12 protocol on TPSS-D3(BJ)/def2-TZVP optimised geometries without spin–orbit and DBOC. We follow the nomenclature of the GMTKN55 [24] database. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		DSDBLYP		B3LYP		PW6B95		PBE	
#	Ref.	D4	D3	D4	D3	D4	D3	D4	D3
N3H5_1–N3H5_2	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.2	1.2
N3H5_1–N3H5_3	5.3	5.3	5.4	5.2	5.3	5.2	5.2	5.6	5.6
N4H6_1–N4H6_2	0.1	0.5	0.5	0.6	0.6	0.8	0.9	0.4	0.4
N4H6_1–N4H6_3	2.3	2.7	2.7	3.0	3.1	3.2	3.2	3.0	3.0
N3P3H12_1–N3P3H12_2	12.2	12.5	12.5	12.2	12.3	12.2	12.2	11.9	11.9
SI5H12_1–SI5H12_2	0.1	−0.1	0.0	0.1	0.2	−0.1	0.0	0.1	0.2
SI5H12_1–SI5H12_3	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	0.9
SI5H12_1–SI5H12_4	3.5	3.7	3.7	3.3	3.3	3.5	3.4	3.1	3.1
SI6H12_1–SI6H12_2	1.7	1.8	1.8	1.7	1.5	1.4	1.4	1.6	1.4
P7H7_1–P7H7_2	1.4	1.6	1.6	1.6	1.6	1.5	1.6	1.2	1.2
S4O4_1–S4O4_2	4.4	4.5	4.5	4.2	4.3	3.8	3.9	5.0	5.0
S8_1–S8_2	9.2	9.1	9.1	9.4	9.1	9.1	9.2	10.3	10.0
H2S2O7_1–H2S2O7_2	0.6	0.5	0.5	0.6	0.6	0.6	0.6	0.5	0.4
H2S2O7_1–H2S2O7_3	3.5	3.2	3.2	3.1	3.2	3.6	3.6	3.1	3.2
H4P2O7_1–H4P2O7_2	1.3	1.4	1.4	1.2	1.2	1.2	1.2	1.2	1.2
H4P2O7_1–H4P2O7_3	3.7	3.4	3.4	3.0	3.0	3.6	3.6	3.8	3.8
H4P2O7_1–H4P2O7_4	4.3	3.7	3.7	3.2	3.4	4.5	4.4	4.2	4.3
MD		0.0	0.0	−0.1	−0.1	0.0	0.0	0.1	0.1
MAD		0.2	0.2	0.3	0.3	0.2	0.2	0.3	0.3
RMSD		0.3	0.3	0.4	0.4	0.3	0.3	0.4	0.4
SD		1.1	1.1	1.7	1.6	1.4	1.4	1.6	1.5
Var		0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.1
Max		0.4	0.4	0.7	0.8	0.8	0.9	1.1	0.8
Min		−0.7	−0.6	−1.1	−1.0	−0.6	−0.5	−0.4	−0.4
AMax		0.7	0.6	1.1	1.0	0.8	0.9	1.1	0.8

N. Statistical evaluation: UPU23

Table A22: Reference values are obtained at the DLPNO-CCSD(T)/CBS*//TPSS-D3(BJ)/def2-TZVP(COSMO) level of theory. We follow the nomenclature of the GMTKN55 [24] database. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		DSDBLYP		B3LYP		PW6B95		PBE	
#	Ref.	D4	D3	D4	D3	D4	D3	D4	D3
2p–1a	4.9	5.4	5.5	5.6	6.0	6.0	6.1	5.5	5.7
2p–1b	3.0	3.7	3.8	3.6	4.1	4.2	4.3	4.0	4.2
2p–1c	8.9	9.4	9.6	9.7	10.1	10.4	10.6	9.6	9.8
2p–1g	2.2	2.6	2.6	2.7	2.7	3.2	3.2	2.9	2.9
2p–1p	2.0	2.7	2.8	2.4	2.7	3.0	3.0	2.5	2.6
2p–2a	3.1	3.0	3.0	3.5	3.5	2.9	2.9	3.1	3.1
2p–5z	0.6	0.2	0.4	−0.3	0.1	0.9	0.9	0.8	1.0
2p–6p	3.3	3.2	3.2	3.1	3.2	3.0	3.1	2.9	2.9
2p–7a	7.3	8.4	8.4	8.8	8.8	8.4	8.4	8.9	8.9
2p–aa	4.0	4.4	4.4	4.8	4.9	4.2	4.2	5.0	5.2
2p–1e	11.1	11.8	11.8	11.8	12.0	12.2	12.3	11.7	11.9
2p–0a	4.8	5.9	6.0	6.0	6.2	5.7	5.8	5.6	5.7
2p–1f	14.4	14.1	14.1	14.3	14.4	14.1	14.2	13.8	13.9
2p–9a	5.2	5.5	5.5	5.8	5.7	5.5	5.4	5.7	5.7
2p–4b	5.5	5.6	5.6	5.5	5.6	5.7	5.7	5.3	5.4
2p–3a	6.8	7.2	7.2	7.3	7.3	7.6	7.6	6.7	6.7
2p–7p	3.9	3.7	3.7	3.6	3.6	3.5	3.5	3.5	3.5
2p–8d	6.4	6.4	6.5	6.7	6.8	6.4	6.5	6.5	6.6
2p–3d	5.4	5.5	5.5	5.7	5.8	5.7	5.8	5.6	5.7
2p–0b	6.7	6.5	6.5	6.1	6.2	6.3	6.3	5.9	6.0
2p–1m	5.6	6.8	6.8	6.7	6.7	6.7	6.7	5.9	5.9
2p–2h	10.4	10.9	10.9	11.5	11.4	10.7	10.8	10.4	10.4
2p–3b	6.1	6.5	6.5	6.4	6.4	6.6	6.6	6.2	6.2
MD		0.3	0.4	0.4	0.6	0.5	0.5	0.3	0.4
MAD		0.4	0.5	0.6	0.7	0.6	0.7	0.5	0.6
RMSD		0.6	0.6	0.7	0.8	0.8	0.8	0.6	0.7
SD		2.1	2.2	2.7	2.8	2.8	2.9	2.8	2.9
Var		0.2	0.2	0.3	0.3	0.4	0.4	0.3	0.4
Max		1.2	1.2	1.5	1.6	1.5	1.7	1.6	1.7
Min		−0.3	−0.3	−0.9	−0.5	−0.4	−0.4	−0.8	−0.8
AMax		1.2	1.2	1.5	1.6	1.5	1.7	1.6	1.7

O. Statistical evaluation: ROT34

Table A23: Statistical data for the results of the ROT34 test set for three DFAs using the def2–QZVP basis set. Anharmonic corrections have been performed at the HF/DZ level of theory as described in the literature [25]. All values are given in MHz. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

			PBE0		PBE		TPSS	
#	rot. const	Ref.	D3	D4	D3	D4	D3	D4
	A	4293.9	4299.8	4298.1	4240.8	4238.8	4235.9	4235.8
1	B	1395.9	1400.7	1400.7	1383.9	1382.9	1384.5	1384.1
	C	1130.2	1133.1	1132.9	1119.3	1118.3	1119.5	1119.1
	A	3322.5	3309.3	3307.7	3247.0	3247.8	3239.0	3240.4
2	B	719.8	718.8	719.0	707.2	707.5	709.5	709.4
	C	698.0	697.0	697.2	686.0	686.0	687.7	687.6
	A	3071.1	3071.9	3071.3	3023.0	3022.8	3021.0	3022.3
3	B	1285.0	1289.9	1290.4	1271.9	1270.9	1271.1	1270.2
	C	1248.7	1249.0	1249.3	1232.4	1231.7	1231.0	1230.7
	A	2755.9	2765.6	2765.8	2731.3	2731.7	2729.3	2730.3
4	B	2675.6	2689.5	2689.3	2652.4	2652.1	2653.3	2653.1
	C	2653.3	2666.5	2666.8	2631.5	2631.8	2633.1	2634.1
5	A	2336.9	2339.1	2339.9	2307.0	2306.5	2306.0	2307.1
	A	1464.2	1471.0	1471.1	1440.0	1439.7	1439.1	1439.9
6	B	768.2	767.6	768.3	756.4	757.1	762.1	763.0
	C	580.6	580.9	581.4	572.3	572.7	576.1	576.8
	A	1165.7	1170.2	1170.4	1152.1	1153.5	1154.6	1155.9
7	B	661.2	660.6	661.3	653.3	653.8	654.0	654.6
	C	454.0	454.6	454.9	448.9	449.4	449.6	450.2
	A	1166.3	1167.7	1168.3	1147.9	1148.4	1153.1	1155.3
8	B	767.6	766.4	767.0	752.7	753.0	754.3	755.0
	C	513.0	512.5	512.9	504.3	504.5	505.6	506.4
	A	862.5	865.9	866.0	852.4	852.4	853.2	853.8
9	B	754.2	752.8	752.8	741.8	741.7	742.6	742.9
	C	513.7	513.6	513.7	505.7	505.6	506.5	506.8
	A	3086.2	3101.0	3100.5	3060.2	3059.9	3061.3	3061.6
10	B	723.7	725.3	725.2	716.2	715.9	715.8	716.0
	C	685.0	686.7	686.6	678.0	677.8	677.7	677.9
	A	1432.1	1436.0	1435.5	1416.5	1416.5	1418.6	1418.9
11	B	820.5	822.8	822.9	810.9	811.4	812.1	813.3
	C	679.4	683.0	682.9	674.1	675.0	675.4	676.1
	A	1523.2	1523.3	1521.2	1496.3	1495.8	1497.2	1497.4
12	B	1070.5	1075.0	1076.0	1059.8	1060.6	1060.9	1061.9
	C	719.9	721.1	721.5	709.3	709.7	711.0	711.9
MD			2.6	2.7	−18.1	−18.1	−17.6	−17.0
MAD			3.8	3.9	18.1	18.1	17.6	17.0
RMSD			5.7	5.8	23.3	23.4	24.1	23.7
SD			29.4	30.0	85.5	86.5	96.5	95.9
Var			26.1	27.3	221.8	226.5	282.2	278.9
Max			14.8	14.3	−5.1	−4.4	−4.0	−3.3
Min			−13.2	−14.8	−75.5	−74.7	−83.5	−82.1
AMax			14.8	14.8	75.5	74.7	83.5	82.1

Table A24: Statistical data for the results of the ROT34 test set for three DFAs using the def2–QZVP basis set. Anharmonic corrections have been performed at the HF/DZ level of theory as described in the literature [25]. All values are given in MHz. We abbreviate D3(BJ)-ATM by D3 and D4(TB)-ATM by D4.

			PBE0		PBE		TPSS	
#	rot. const	Ref.	D3	D4	D3	D4	D3	D4
	A	4293.9	4299.8	4300.5	4240.8	4239.3	4235.9	4239.0
1	B	1395.9	1400.7	1400.3	1383.9	1383.6	1384.5	1384.9
	C	1130.2	1133.1	1132.8	1119.3	1118.8	1119.5	1119.9
	A	3322.5	3309.3	3308.4	3247.0	3247.9	3239.0	3243.4
2	B	719.8	718.8	718.9	707.2	708.0	709.5	710.5
	C	698.0	697.0	697.1	686.0	686.3	687.7	688.3
	A	3071.1	3071.9	3072.6	3023.0	3023.1	3021.0	3024.1
3	B	1285.0	1289.9	1290.0	1271.9	1271.9	1271.1	1272.3
	C	1248.7	1249.0	1248.8	1232.4	1232.0	1231.0	1231.8
	A	2755.9	2765.6	2766.1	2731.3	2732.3	2729.3	2732.0
4	B	2675.6	2689.5	2689.8	2652.4	2652.8	2653.3	2654.7
	C	2653.3	2666.5	2667.2	2631.5	2632.2	2633.1	2635.1
5	A	2336.9	2339.1	2339.1	2307.0	2307.1	2306.0	2308.6
	A	1464.2	1471.0	1471.4	1440.0	1440.2	1439.1	1440.7
6	B	768.2	767.6	768.5	756.4	757.3	762.1	764.5
	C	580.6	580.9	581.5	572.3	572.8	576.1	577.9
	A	1165.7	1170.2	1170.1	1152.1	1153.4	1154.6	1156.2
7	B	661.2	660.6	661.0	653.3	653.8	654.0	654.7
	C	454.0	454.6	454.8	448.9	449.4	449.6	450.2
	A	1166.3	1167.7	1168.3	1147.9	1149.6	1153.1	1158.8
8	B	767.6	766.4	766.9	752.7	753.3	754.3	755.8
	C	513.0	512.5	512.8	504.3	504.8	505.6	507.2
	A	862.5	865.9	866.0	852.4	852.6	853.2	854.7
9	B	754.2	752.8	752.8	741.8	741.9	742.6	743.6
	C	513.7	513.6	513.7	505.7	505.8	506.5	507.3
	A	3086.2	3101.0	3100.8	3060.2	3060.5	3061.3	3063.5
10	B	723.7	725.3	725.3	716.2	716.1	715.8	716.6
	C	685.0	686.7	686.6	678.0	677.9	677.7	678.5
	A	1432.1	1436.0	1435.6	1416.5	1416.4	1418.6	1421.2
11	B	820.5	822.8	822.6	810.9	810.9	812.1	813.2
	C	679.4	683.0	682.7	674.1	674.1	675.4	676.3
	A	1523.2	1523.3	1520.1	1496.3	1495.5	1497.2	1499.0
12	B	1070.5	1075.0	1076.4	1059.8	1060.6	1060.9	1062.5
	C	719.9	721.1	721.5	709.3	710.1	711.0	712.7
MD			2.6	2.7	−18.1	−17.8	−17.6	−15.8
MAD			3.8	4.0	18.1	17.8	17.6	15.8
RMSD			5.7	5.9	23.3	23.1	24.1	22.4
SD			29.4	30.6	85.5	86.0	96.5	92.7
Var			26.1	28.3	221.8	224.3	282.2	260.3
Max			14.8	14.6	−5.1	−4.6	−4.0	−2.7
Min			−13.2	−14.1	−75.5	−74.6	−83.5	−79.1
AMax			14.8	14.6	75.5	74.6	83.5	79.1

P. Statistical evaluation: LMGB35

Table A25: The LMGB35 benchnmark set contains of systems from the first and second row of the periodic system. All bond lengths are given in pm. Reference distances are taken from Ref. [26].We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
H_2(H–H)	74.1	74.5	74.4	75.0	75.0	74.3	74.2
HF(H–F)	91.7	91.8	91.7	93.0	93.0	92.9	92.9
H_2O(HO)	95.7	95.7	95.7	96.9	96.9	96.7	96.7
HOF(OH)	96.6	96.6	96.6	97.9	97.9	97.7	97.7
OH(O–H)	97.0	97.0	97.0	98.3	98.3	98.2	98.1
NH_3(N–H)	101.2	101.1	101.1	102.1	102.1	101.9	101.8
OH^+(O–H)	102.9	103.2	103.2	104.7	104.7	104.0	103.9
NH(N–H)	103.6	103.7	103.7	105.0	104.9	104.4	104.4
C_2H_2(C–H)	106.2	106.4	106.4	107.0	107.0	106.5	106.5
NO^+(N–O)	106.3	105.3	105.3	106.9	106.9	106.6	106.6
HCN(H–C)	106.5	106.8	106.8	107.5	107.5	107.0	107.0
NH^+(N–H)	107.0	107.6	107.6	109.1	109.1	108.3	108.3
C_2H_4(C–H)	108.1	108.3	108.3	109.1	109.1	108.6	108.6
CH_4(CH)	108.6	108.8	108.8	109.5	109.5	109.1	109.1
N_2(N–N)	109.8	108.9	108.9	110.2	110.2	109.9	109.9
CH_2O(O–H)	109.9	110.7	110.7	111.7	111.7	111.0	111.0
N_2^+(N–N)	111.6	110.1	110.1	111.4	111.4	111.2	111.2
O_2^+(O–O)	111.6	109.8	109.8	112.1	112.1	112.0	112.0
CH(C–H)	112.0	112.4	112.4	113.6	113.6	112.9	112.9
CO(C–O)	112.8	112.2	112.2	113.5	113.5	113.3	113.3
HCN(C–N)	115.3	114.5	114.5	115.7	115.7	115.4	115.4
CO_2(C–O)	116.0	115.6	115.6	117.0	117.0	116.8	116.8
C_2H_2(C–C)	120.3	119.6	119.6	120.6	120.6	120.2	120.2
CH_2O(C–O)	120.3	119.5	119.5	120.8	120.8	120.7	120.7
BO(B–O)	120.5	119.9	119.9	121.3	121.3	121.2	121.2
O_2(O–O)	120.8	119.2	119.2	121.8	121.8	121.9	121.9
BH(B–H)	123.2	124.0	124.0	125.1	125.1	123.6	123.6
BF(B–F)	126.3	125.9	125.9	127.3	127.3	127.3	127.3
CF(C–F)	127.2	126.7	126.7	128.5	128.5	128.9	128.9
NF(N–F)	131.7	130.3	130.3	132.7	132.7	133.3	133.3
F_2^+(F–F)	132.2	127.2	127.3	131.6	131.6	131.7	131.7
C_2H_4(C–C)	133.4	132.2	132.2	133.2	133.2	133.0	133.0
F_2(F–F)	141.2	137.5	137.6	141.4	141.4	141.6	141.6
HOF(O–F)	143.5	140.5	140.6	144.5	144.5	145.0	145.0
B2(B–B)	159.0	161.3	161.3	161.8	161.8	161.9	161.9
MD		−0.5	−0.6	1.0	1.0	0.7	0.7
MAD		0.9	0.9	1.0	1.0	0.8	0.8
RMSD		1.4	1.4	1.2	1.2	1.0	1.0
SD		7.8	7.7	4.0	3.9	3.9	3.9
Var		1.8	1.7	0.5	0.5	0.5	0.5
Max		2.3	2.3	2.8	2.8	2.9	2.9
Min		−5.0	−4.9	−0.6	−0.6	−0.5	−0.5
AMax		5.0	4.9	2.8	2.8	2.9	2.9

Table A26: The LMGB35 benchnmark set contains of systems from the first and second row of the periodic system. All bond lengths are given in pm. Reference distances are taken from Ref. [26].We abbreviate D3(BJ)-ATM by D3 and D4(TB)-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
H_2(H–H)	74.1	74.5	74.4	75.0	74.2	74.3	74.2
HF(H–F)	91.7	91.8	91.7	93.0	92.9	92.9	92.9
H_2O(HO)	95.7	95.7	95.7	96.9	96.7	96.7	96.7
HOF(OH)	96.6	96.6	96.6	97.9	97.7	97.7	97.7
OH(O–H)	97.0	97.0	97.0	98.3	98.1	98.2	98.1
NH_3(N–H)	101.2	101.1	101.1	102.1	101.9	101.9	101.9
OH^+(O–H)	102.9	103.2	103.2	104.7	103.9	104.0	103.9
NH(N–H)	103.6	103.7	103.7	105.0	104.4	104.4	104.4
C_2H_2(C–H)	106.2	106.4	106.4	107.0	106.5	106.5	106.5
NO^+(N–O)	106.3	105.3	105.3	106.9	106.6	106.6	106.6
HCN(H–C)	106.5	106.8	106.8	107.5	107.0	107.0	107.0
NH^+(N–H)	107.0	107.6	107.6	109.1	108.3	108.3	108.3
C_2H_4(C–H)	108.1	108.3	108.3	109.1	108.6	108.6	108.6
CH_4(CH)	108.6	108.8	108.8	109.5	109.1	109.1	109.1
N_2(N–N)	109.8	108.9	108.9	110.2	109.9	109.9	109.9
CH_2O(O–H)	109.9	110.7	110.7	111.7	111.0	111.0	111.0
N_2^+(N–N)	111.6	110.1	110.1	111.4	111.2	111.2	111.2
O_2^+(O–O)	111.6	109.8	109.8	112.1	112.0	112.0	112.0
CH(C–H)	112.0	112.4	112.4	113.6	112.9	112.9	112.9
CO(C–O)	112.8	112.2	112.2	113.5	113.3	113.3	113.3
HCN(C–N)	115.3	114.5	114.5	115.7	115.4	115.4	115.4
CO_2(C–O)	116.0	115.6	115.6	117.0	116.8	116.8	116.8
C_2H_2(C–C)	120.3	119.6	119.6	120.6	120.2	120.2	120.2
CH_2O(C–O)	120.3	119.5	119.5	120.8	120.7	120.7	120.7
BO(B–O)	120.5	119.9	119.9	121.3	121.2	121.2	121.2
O_2(O–O)	120.8	119.2	119.2	121.8	121.9	121.9	121.9
BH(B–H)	123.2	124.0	124.0	125.1	123.6	123.6	123.6
BF(B–F)	126.3	125.9	125.9	127.3	127.3	127.3	127.3
CF(C–F)	127.2	126.7	126.7	128.5	128.9	128.9	128.9
NF(N–F)	131.7	130.3	130.3	132.7	133.3	133.3	133.3
F_2^+(F–F)	132.2	127.2	127.3	131.6	131.7	131.7	131.7
C_2H_4(C–C)	133.4	132.2	132.2	133.2	133.0	133.0	133.0
F_2(F–F)	141.2	137.5	137.6	141.4	141.6	141.6	141.6
HOF(O–F)	143.5	140.5	140.6	144.5	145.0	145.0	145.0
B2(B–B)	159.0	161.3	161.3	161.8	161.9	161.9	161.9
MD		−0.5	−0.6	1.0	0.7	0.7	0.7
MAD		0.9	0.9	1.0	0.8	0.8	0.8
RMSD		1.4	1.4	1.2	1.0	1.0	1.0
SD		7.8	7.7	4.0	3.9	3.9	3.9
Var		1.8	1.7	0.5	0.5	0.5	0.5
Max		2.3	2.3	2.8	2.9	2.9	2.9
Min		−5.0	−4.9	−0.6	−0.5	−0.5	−0.5
AMax		5.0	4.9	2.8	2.9	2.9	2.9

Q. Statistical evaluation: HMGB11

Table A27: Experimental reference bond distances for 11 molecules from Ref. [27] containing third–row or higher main group elements. All distances are given in pm. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
Cl_2(Cl–Cl)	198.8	197.9	197.9	200.4	200.5	200.8	200.8
S_2H_2(S–S)	205.5	204.4	204.4	206.3	206.3	206.4	206.4
$P_2(CH_3)_4$(P–P)	221.2	219.2	219.2	221.3	221.4	220.9	221.0
Br_2(Br–Br)	228.1	227.8	227.8	230.8	230.8	230.5	230.5
Se_2H_2(Se–Se)	234.6	232.4	232.4	235.0	235.0	234.4	234.4
Ge_2H_6(Ge–Ge)	241.0	242.1	242.1	243.3	243.3	242.5	242.5
$As_2(CH_3)_4$(As–As)	242.9	243.8	243.8	247.3	247.2	246.1	246.1
$Te_2(CH_3)_2$(Te–Te)	268.6	267.3	267.3	269.7	269.6	268.5	269.1
$Sn_2(CH_3)_6$(Sn–Sn)	277.6	277.7	278.0	279.6	280.1	278.4	278.9
$Sb_2(CH_3)_4$(Sb–Sb)	281.8	282.5	282.6	286.2	286.1	284.9	285.0
$Pb_2(CH_3)_6$(Pb–Pb)	288.0	287.1	287.2	292.0	291.9	289.8	290.3
MD		−0.5	−0.5	2.2	2.2	1.4	1.5
MAD		1.0	1.1	2.2	2.2	1.5	1.6
RMSD		1.2	1.2	2.6	2.6	1.8	1.9
SD		3.6	3.6	4.9	4.8	4.0	3.8
Var		1.3	1.3	2.4	2.3	1.6	1.5
Max		1.1	1.1	4.4	4.3	3.2	3.2
Min		−2.2	−2.2	0.1	0.2	−0.3	−0.2
AMax		2.2	2.2	4.4	4.3	3.2	3.2

Table A28: Experimental reference bond distances for 11 molecules from Ref. [27] containing third–row or higher main group elements. All distances are given in pm. We abbreviate D3(BJ)-ATM by D3 and D4(TB)-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
Cl_2(Cl–Cl)	198.8	197.9	197.9	200.4	200.5	200.8	200.8
S_2H_2(S–S)	205.5	204.4	204.4	206.3	206.4	206.4	206.4
$P_2(CH_3)_4$(P–P)	221.2	219.2	219.2	221.3	221.7	220.9	221.3
Br_2(Br–Br)	228.1	227.8	227.8	230.8	230.8	230.5	230.6
Se_2H_2(Se–Se)	234.6	232.4	232.4	235.0	235.0	234.4	234.5
Ge_2H_6(Ge–Ge)	241.0	242.1	242.1	243.3	243.3	242.5	242.6
$As_2(CH_3)_4$(As–As)	242.9	243.8	243.8	247.3	247.4	246.1	246.3
$Te_2(CH_3)_2$(Te–Te)	268.6	267.3	267.3	269.7	269.8	268.5	269.2
$Sn_2(CH_3)_6$(Sn–Sn)	277.6	277.7	278.0	279.6	280.7	278.4	279.3
$Sb_2(CH_3)_4$(Sb–Sb)	281.8	282.5	282.6	286.2	286.8	284.9	285.5
$Pb_2(CH_3)_6$(Pb–Pb)	288.0	287.1	287.2	292.0	292.7	289.8	291.0
MD		−0.5	−0.5	2.2	2.4	1.4	1.8
MAD		1.0	1.1	2.2	2.4	1.5	1.8
RMSD		1.2	1.2	2.6	2.9	1.8	2.1
SD		3.6	3.6	4.9	5.3	4.0	4.1
Var		1.3	1.3	2.4	2.9	1.6	1.7
Max		1.1	1.1	4.4	5.0	3.2	3.7
Min		−2.2	−2.2	0.1	0.4	−0.3	−0.1
AMax		2.2	2.2	4.4	5.0	3.2	3.7

R. Statistical evaluation: TMC32

Table A29: Diverse set of 32 metal complexes from the first transition row, for which precise gas-phase geometries are known from electron diffraction or microwave spectroscopy. Compilation by Bühl *et al.* [28]. We abbreviate D3(BJ)-ATM by D3 and D4-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
$Sc(acac)_3$(Sc–O)	207.6	209.0	208.8	210.4	210.3	210.0	209.8
$TiCl_4$(Ti–Cl)	216.9	216.4	216.4	218.3	218.2	218.3	218.3
$Ti(CH_3)Cl_3$(Ti–C)	204.7	202.3	202.3	204.5	204.7	205.3	205.3
$Ti(CH_3)Cl_3$(Ti–Cl)	218.5	218.0	217.9	219.3	219.2	219.5	219.4
$Ti(CH_3)_2Cl_2$(Ti–C)	205.8	203.5	203.6	205.5	205.5	206.3	206.3
$Ti(CH_3)_2Cl_2$(Ti–Cl)	219.6	219.6	219.6	220.5	220.4	220.7	220.6
$Ti(BD_4)_3$(Ti–B)	217.5	214.3	214.3	214.7	214.6	214.9	214.8
$Ti(BD_4)_3$(Ti–D^{br})	198.4	193.4	193.5	193.7	193.7	193.2	193.1
VOF_3(V=O)	157.0	154.1	154.1	157.5	157.5	157.6	157.5
VOF_3(V–F)	172.9	171.6	171.6	173.7	173.7	173.4	173.4
VF_5(V–F^{ax})	173.4	173.5	173.5	176.4	176.4	175.9	175.9
VF_5(V–F^{eq})	170.8	169.9	169.9	172.7	172.6	172.3	172.3
$VOCl_3$(V=O)	157.3	153.9	153.9	157.2	157.2	157.3	157.3
$VOCl_3$(V–Cl)	213.8	213.0	213.0	215.0	214.9	214.9	214.9
$V(N(CH_3)_2)_4$(V–N)	187.9	186.1	186.1	188.2	188.1	188.1	187.9
$V(Cp)(CO)_4$(V–C^{CO})	196.3	192.3	192.3	192.7	192.7	194.4	194.3
CrO_2F_2(Cr=O)	157.4	153.7	153.6	157.1	157.1	157.0	157.0
CrO_2F_2(Cr–F)	171.9	170.2	170.2	172.4	172.3	172.0	172.0
CrO_2Cl_2(Cr=O)	157.7	153.8	153.8	157.2	157.2	157.2	157.1
CrO_2Cl_2(Cr–Cl)	212.2	210.6	210.6	212.4	212.4	212.4	212.3
$CrO_2(NO_3)_2$(Cr=O)	158.4	153.8	153.8	157.4	157.4	157.4	157.4
$CrO_2(NO_3)_2$(Cr–O)	195.4	191.0	191.0	193.2	193.2	193.0	192.9
$Cr(C_6H_6)_2$(Cr–C)	215.0	213.0	212.9	213.8	213.7	213.6	213.5
$Cr(C_6H_6)(CO)_3$(Cr–C^{Ar})	220.8	219.1	219.2	221.0	221.1	220.2	220.2
$Cr(C_6H_6)(CO)_3$(Cr–C^{CO})	186.3	183.8	183.8	183.9	183.9	185.2	185.0
$Cr(NO)_4$(Cr–N)	175.0	171.5	171.5	174.1	174.1	174.1	174.0
MnO_3F(Mn=O)	158.6	154.2	154.2	159.2	157.7	157.6	157.6
MnO_3F(Mn–F)	172.4	170.1	170.1	171.0	172.0	171.6	171.6
$MnCp(CO)_3$(Mn–C^{Cp})	214.7	213.7	213.7	215.2	215.1	214.3	214.2
$MnCp(CO)_3$(Mn–C^{CO})	180.6	178.3	178.3	178.4	178.3	179.4	179.3
$Fe(CO)_5$(Fe–C)^{mean}	182.9	179.7	179.7	180.2	180.1	181.0	180.9
$Fe(CO)_3$(tmm)(Fe–C^{CO})	181.0	177.9	177.9	178.0	178.0	178.8	178.8
$Fe(CO)_3$(tmm)(Fe–C^{cent})	193.8	192.2	192.2	194.6	194.6	194.3	194.3
$Fe(CO)_3$(tmm)(Fe–C^{CH_2})	212.3	209.8	209.9	213.1	213.2	212.0	212.2
$Fe(CO)_2(NO)_2$(Fe–C)^{mean}	187.2	180.8	180.8	181.5	181.3	182.3	182.2
$Fe(CO)_2(NO)_2$(Fe–N)	167.4	164.1	164.1	167.1	167.0	166.9	166.9
$FeCp_2$(Fe–C)	206.4	204.2	204.2	204.0	204.1	203.7	203.5
$Fe(C_2H_4)(CO)_4$(Fe–C^{et})	211.7	209.7	216.2	213.0	216.7	212.3	216.7
$Fe(C_2H_4)(CO)_4$(Fe–C^{ax})	181.5	180.0	180.1	179.9	179.9	180.7	180.7
$Fe(C_2H_4)(CO)_4$(Fe–C^{eq})	180.6	178.1	177.8	178.9	178.7	179.6	179.3
$Fe(C_5(CH_3)_5)(P_5)$(Fe–P)	237.7	235.7	235.7	236.3	236.1	234.9	234.7
$CoH(CO)_4$(Co–C^{eq})	181.8	178.4	178.4	179.0	179.0	179.5	179.5
$Co(CO)_3(NO)$(Co–N)	165.8	162.9	162.9	166.1	166.1	165.8	165.8
$Co(CO)_3(NO)$(Co–C)	183.0	180.1	180.1	180.5	180.4	181.1	181.0
$Ni(CO)_4$(Ni–C)	182.5	182.1	182.0	182.3	182.2	182.7	182.6
$Ni(acac)_2$(Ni–O)	187.6	185.1	184.3	185.8	185.3	185.4	184.6
$Ni(PF_3)_4$(Ni–P)	209.9	209.0	208.8	210.6	210.3	210.0	209.5
$CuCH_3$(Cu–C)	188.4	190.1	190.1	189.3	189.4	189.6	189.6
CuCN(Cu–C)	183.2	184.3	184.3	182.0	182.0	182.3	182.3
$Cu(acac)_2$(Cu–O)	191.4	191.9	191.8	194.3	194.2	193.2	193.1
MD		−2.1	−2.0	−0.6	−0.5	−0.6	−0.5
MAD		2.3	2.4	1.5	1.6	1.3	1.4
RMSD		2.7	2.8	1.9	2.1	1.7	1.9
SD		11.6	13.3	13.0	14.0	11.3	12.8
Var		2.7	3.6	3.5	4.0	2.6	3.3
Max		1.7	4.5	3.0	5.0	2.5	5.0
Min		−6.4	−6.4	−5.7	−5.9	−5.2	−5.3
AMax		6.4	6.4	5.7	5.9	5.2	5.3

Table A30: Diverse set of 32 metal complexes from the first transition row, for which precise gas-phase geometries are known from electron diffraction or microwave spectroscopy. Compilation by Bühl *et al.* [28]. We abbreviate D3(BJ)-ATM by D3 and D4(TB)-ATM by D4.

		PBE0		PBE		TPSS	
system(bond)	Ref.	D3	D4	D3	D4	D3	D4
$Sc(acac)_3$(Sc–O)	207.6	209.0	208.9	210.4	210.3	210.0	209.8
$TiCl_4$(Ti–Cl)	216.9	216.4	216.4	218.3	218.2	218.3	218.3
$Ti(CH_3)Cl_3$(Ti–C)	204.7	202.3	202.3	204.5	204.5	205.3	205.4
$Ti(CH_3)Cl_3$(Ti–Cl)	218.5	218.0	217.9	219.3	219.3	219.5	219.5
$Ti(CH_3)_2Cl_2$(Ti–C)	205.8	203.5	203.6	205.5	205.5	206.3	206.4
$Ti(CH_3)_2Cl_2$(Ti–Cl)	219.6	219.6	219.5	220.5	220.5	220.7	220.7
$Ti(BD_4)_3$(Ti–B)	217.5	214.3	214.3	214.7	214.6	214.9	214.8
$Ti(BD_4)_3$(Ti–D^{br})	198.4	193.4	193.4	193.7	193.7	193.2	193.1
VOF_3(V=O)	157.0	154.1	154.1	157.5	157.5	157.6	157.5
VOF_3(V–F)	172.9	171.6	171.6	173.7	173.7	173.4	173.4
VF_5(V–F^{ax})	173.4	173.5	173.5	176.4	176.4	175.9	175.9
VF_5(V–F^{eq})	170.8	169.9	169.8	172.7	172.6	172.3	172.4
$VOCl_3$(V=O)	157.3	153.9	153.9	157.2	157.2	157.3	157.3
$VOCl_3$(V–Cl)	213.8	213.0	213.0	215.0	214.9	214.9	214.9
$V(N(CH_3)_2)_4$(V–N)	187.9	186.1	186.2	188.2	188.1	188.1	188.0
$V(Cp)(CO)_4$(V–C^{CO})	196.3	192.3	192.3	192.7	192.7	194.4	194.3
CrO_2F_2(Cr=O)	157.4	153.7	153.7	157.1	157.1	157.0	157.0
CrO_2F_2(Cr–F)	171.9	170.2	170.2	172.4	172.4	172.0	172.0
CrO_2Cl_2(Cr=O)	157.7	153.8	153.8	157.2	157.2	157.2	157.2
CrO_2Cl_2(Cr–Cl)	212.2	210.6	210.6	212.4	212.4	212.4	212.4
$CrO_2(NO_3)_2$(Cr=O)	158.4	153.8	153.8	157.4	157.4	157.4	157.4
$CrO_2(NO_3)_2$(Cr–O)	195.4	191.0	191.0	193.2	193.2	193.0	192.9
$Cr(C_6H_6)_2$(Cr–C)	215.0	213.0	213.0	213.8	213.7	213.6	213.6
$Cr(C_6H_6)(CO)_3$(Cr–C^{Ar})	220.8	219.1	219.2	221.0	221.1	220.2	220.3
$Cr(C_6H_6)(CO)_3$(Cr–C^{CO})	186.3	183.8	183.8	183.9	183.9	185.2	185.1
$Cr(NO)_4$(Cr–N)	175.0	171.5	171.5	174.1	174.1	174.1	174.1
MnO_3F(Mn=O)	158.6	154.2	154.2	159.2	157.7	157.6	157.6
MnO_3F(Mn–F)	172.4	170.1	170.1	171.0	172.0	171.6	171.6
$MnCp(CO)_3$(Mn–C^{Cp})	214.7	213.7	213.7	215.2	215.1	214.3	214.3
$MnCp(CO)_3$(Mn–C^{CO})	180.6	178.3	178.3	178.4	178.4	179.4	179.4
$Fe(CO)_5$(Fe–C)^{mean}	182.9	179.7	179.7	180.2	180.2	181.0	181.0
$Fe(CO)_3$(tmm)(Fe–C^{CO})	181.0	177.9	177.9	178.0	178.0	178.8	178.8
$Fe(CO)_3$(tmm)(Fe–C^{cent})	193.8	192.2	192.2	194.6	194.7	194.3	194.4
$Fe(CO)_3$(tmm)(Fe–C^{CH_2})	212.3	209.8	209.8	213.1	213.1	212.0	212.2
$Fe(CO)_2(NO)_2$(Fe–C)^{mean}	187.2	180.8	180.7	181.5	181.4	182.3	182.3
$Fe(CO)_2(NO)_2$(Fe–N)	167.4	164.1	164.2	167.1	167.1	166.9	166.9
$FeCp_2$(Fe–C)	206.4	204.2	204.2	204.0	204.1	203.7	203.6
$Fe(C_2H_4)(CO)_4$(Fe–C^{et})	211.7	209.7	209.9	213.0	213.1	212.3	212.6
$Fe(C_2H_4)(CO)_4$(Fe–C^{ax})	181.5	180.0	180.0	179.9	179.9	180.7	180.7
$Fe(C_2H_4)(CO)_4$(Fe–C^{eq})	180.6	178.1	178.1	178.9	178.8	179.6	179.6
$Fe(C_5(CH_3)_5)(P_5)$(Fe–P)	237.7	235.7	244.7	236.3	236.2	234.9	234.8
$CoH(CO)_4$(Co–C^{eq})	181.8	178.4	178.4	179.0	179.0	179.5	179.5
$Co(CO)_3(NO)$(Co–N)	165.8	162.9	162.9	166.1	166.1	165.8	165.8
$Co(CO)_3(NO)$(Co–C)	183.0	180.1	180.1	180.5	180.5	181.1	181.1
$Ni(CO)_4$(Ni–C)	182.5	182.1	182.0	182.3	182.3	182.7	182.7
$Ni(acac)_2$(Ni–O)	187.6	185.1	184.3	185.8	185.3	185.4	184.6
$Ni(PF_3)_4$(Ni–P)	209.9	209.0	208.4	210.6	209.8	210.0	209.1
$CuCH_3$(Cu–C)	188.4	190.1	190.1	189.3	189.4	189.6	189.6
CuCN(Cu–C)	183.2	184.3	184.3	182.0	182.0	182.3	182.3
$Cu(acac)_2$(Cu–O)	191.4	191.9	191.8	194.3	194.2	193.2	193.1
MD		−2.1	−2.0	−0.6	−0.6	−0.6	−0.6
MAD		2.3	2.5	1.5	1.5	1.3	1.3
RMSD		2.7	2.9	1.9	1.9	1.7	1.7
SD		11.6	14.7	13.0	12.9	11.3	11.5
Var		2.7	4.4	3.5	3.4	2.6	2.7
Max		1.7	7.0	3.0	3.0	2.5	2.5
Min		−6.4	−6.5	−5.7	−5.8	−5.2	−5.3
AMax		6.4	7.0	5.7	5.8	5.2	5.3

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