

A generally applicable atomic-charge dependent London dispersion correction scheme

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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

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

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

$$E_{\text{IES}} = \mathbf{q}^\top \left(\frac{1}{2} A \mathbf{q} - \mathbf{X} \right) \quad (2)$$

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

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

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

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

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

$$\begin{pmatrix} A & \mathbf{1} \\ \mathbf{1}^\top & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{q} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ q_{\text{total}} \end{pmatrix} \quad (5)$$

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

$$\chi_i = \text{EN}_i - \kappa_i \sqrt{m\text{CN}_i} \quad (6)$$

where EN_i is the electronegativity, κ_i is a scaling factor for the geometry dependency, and $m\text{CN}_i$ is the coordination number defined as

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

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. $R_{ij}^{\text{cov}} = R_i^{\text{cov}} + R_j^{\text{cov}}$ 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

$$\begin{aligned} \frac{\partial L}{\partial q_k} = 0 \quad \implies \quad 0 &= \frac{d}{d\mathbf{R}_j} \frac{\partial L}{\partial q_k} = \frac{\partial^2 L}{\partial q_k \partial \mathbf{R}_j} + \frac{\partial^2 L}{\partial q_k^2} \cdot \frac{\partial q_k}{\partial \mathbf{R}_j} \\ &\iff \frac{\partial^2 L}{\partial q_k^2} \cdot \frac{\partial q_k}{\partial \mathbf{R}_j} = - \frac{\partial^2 L}{\partial q_k \partial \mathbf{R}_j} \end{aligned} \quad (8)$$

Plugging in the expression for L from equation 4 we get

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

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

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

Plugging everything back into equation 8 we get

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

To invert the indefinite but symmetric $(N + 1)$ 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

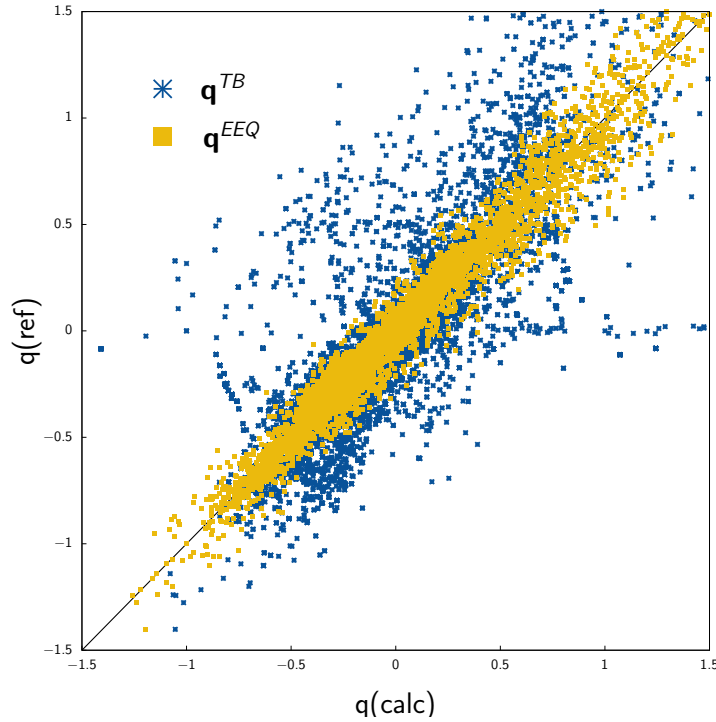


Figure 1: EEQ versus GFN2-xTB partial charges in direct correlation with Hirshfeld partial charges calculated at the PBE0/def2-TZVP level of theory for all elements with $Z = 1 - 86$.

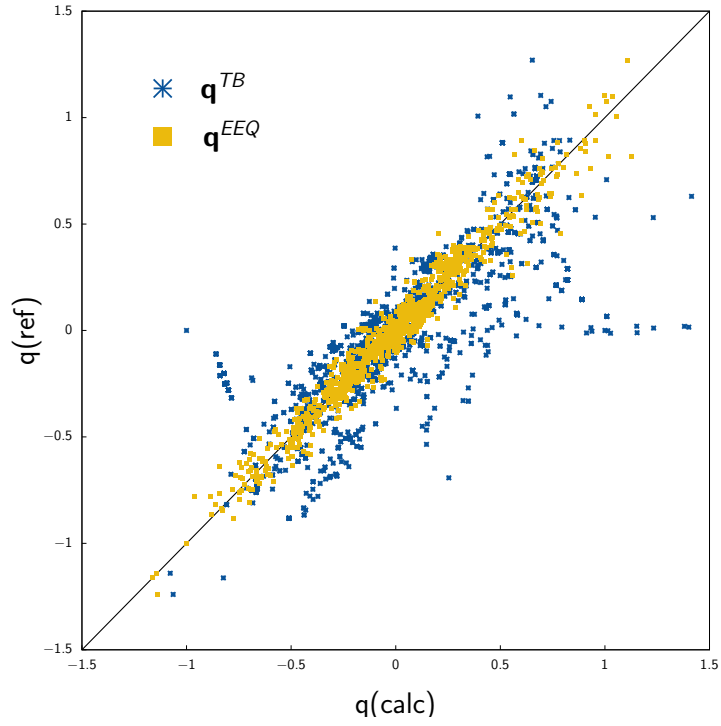


Figure 2: EEQ versus GFN2-xTB partial charges in direct correlation with Hirshfeld partial charges calculated at the PBE0/def2-TZVP level of theory for all elements with $Z = 1 - 17$ (excluding helium and neon).

B. Many-body dispersion theory

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

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

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

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

In equation 13, K and P label atoms, and β and γ refer to the Cartesian components of their inter-nuclear distance. The use of D4 atom-in-molecule dynamic polarizabilities offers advantages. Different from the TS-based polarizabilities, the D4 polarizabilities 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

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

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

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

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

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

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.,

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

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 $E_{\text{disp}}^{(6,8)}$). The second part includes all dipole-dipole interactions up to infinite order, $E_{\text{disp}}^{(n),MBD}$ ($n = 6, 9, 12, 15, \dots, \infty$). To avoid double counting of the two-body dipole-dipole energy, it is removed explicitly from the MBD energy according to

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

Exploiting that $E_{\text{disp}}^{(6)} = E_{\text{disp}}^{(6),MBD}$ and re-arranging to $E_{\text{disp}}^{D4-MBD} = E_{\text{disp}}^{(n),MBD} + E_{\text{disp}}^{(8)}$ 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.

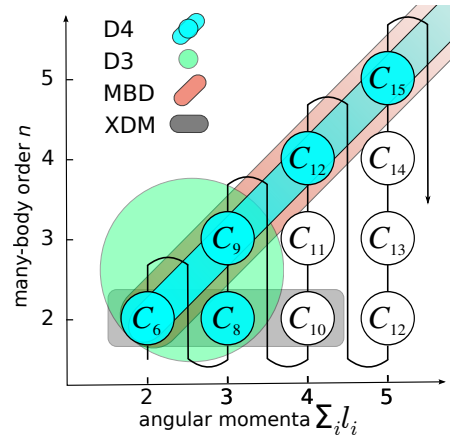


Figure 3: Asymptotic dispersion coefficients from different many-body orders and increasing number of terms in the multipole expansion. The contributions covered by the D3 (including ATM term), D4-MBD, MBD, and XDM methods are highlighted. This Figure is generated in analogy to Figure 16 in Ref.[7].

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

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

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

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

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

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

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

D. Double hybrid density functionals

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

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

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

Name	Exchange	Correlation	a_x^{Fock}	a_c^{DFT}	$a_c^{\text{PT2, OS}}$	$a_c^{\text{PT2, SS}}$	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
B1LYP	1.0000	1.831 272 96	0.385 666 78	4.461 650 03
B1P	1.0000	3.396 277 82	0.483 788 48	5.039 314 38
B3LYP	1.0000	1.934 375 18	0.405 343 40	4.464 808 49
B3P	1.0000	3.164 910 35	0.470 743 24	4.980 269 96
B3PW	1.0000	2.716 412 16	0.444 940 36	4.525 740 06
B97	1.0000	0.898 281 66	0.308 159 53	4.443 432 55
BHLYP	1.0000	1.511 937 99	0.283 526 72	5.306 773 49
BLYP	1.0000	2.291 958 45	0.436 492 21	4.072 641 55
BPBE	1.0000	3.634 727 63	0.471 496 79	4.349 135 93
BP	1.0000	3.099 804 46	0.411 773 21	4.917 601 74
BPW	1.0000	2.945 620 42	0.459 652 20	4.160 801 74
CAMB3LYP	1.0000	1.640 132 69	0.427 834 52	5.006 589 11
HF	1.0000	1.608 199 47	0.448 239 43	3.347 393 36
LB94	1.0000	2.509 510 42	0.375 486 45	3.398 143 97
LCBLYP	1.0000	1.549 120 35	0.641 332 51	7.029 767 07
M062X	1.0000	−0.114 980 52	0.863 983 40	7.324 646 59
M06	1.0000	0.461 795 92	0.588 294 27	5.979 128 83
M06L	1.0000	−0.001 871 13	0.709 904 19	6.044 546 04
MPW1LYP	1.0000	1.325 255 01	0.300 734 71	5.177 786 98
MPW1PW	1.0000	1.622 450 65	0.417 390 65	4.608 984 22
MPWLYP	1.0000	1.358 594 18	0.286 790 77	4.915 528 02
MPWPW	1.0000	1.720 532 69	0.327 445 16	4.821 968 51
O3LYP	1.0000	1.725 418 78	0.108 007 65	6.062 297 94
OLYP	1.0000	2.675 704 77	0.571 499 58	2.618 045 72
OPBE	1.0000	2.900 419 24	0.629 092 63	2.369 558 85
PBE0	1.0000	1.184 525 05	0.419 325 54	4.896 182 46
PBE	1.0000	0.942 433 11	0.407 215 68	4.663 683 52
PW1PW	1.0000	1.175 089 11	0.470 514 91	4.887 113 96
PW6B95	1.0000	−0.235 168 29	0.076 652 68	5.867 151 85
PW86PBE	1.0000	1.436 090 69	0.426 824 22	4.677 535 37
PW91	1.0000	0.857 599 27	0.391 077 40	4.993 347 11
PWP1	1.0000	0.628 305 40	0.556 318 71	5.336 288 63
PWP	1.0000	0.564 310 39	0.475 942 44	5.652 544 49
REVPBE0	1.0000	1.501 411 70	0.358 557 96	4.160 675 32
REVPBE38	1.0000	1.714 571 64	0.387 367 94	4.422 613 01

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
REVPBE	1.0000	1.709 537 50	0.523 485 07	3.087 659 99
REVTPSS	1.0000	1.495 702 30	0.432 205 13	4.664 565 96
RPBE	1.0000	1.288 359 06	0.452 666 03	3.173 210 40
RPW86PBE	1.0000	1.224 742 18	0.399 271 28	4.702 904 60
SCAN	1.0000	0.453 179 23	0.614 878 01	5.891 224 26
TPSS0	1.0000	1.535 123 60	0.397 949 92	4.746 280 72
TPSS	1.0000	2.224 508 11	0.448 852 11	4.649 829 37
TPSSH	1.0000	2.144 052 67	0.453 246 85	4.659 098 65
WB97	1.0000	1.090 578 50	0.748 818 84	7.317 918 71
WB97X	1.0000	0.339 183 75	0.574 225 50	6.435 384 96
X3LYP	1.0000	1.498 323 79	0.212 959 05	5.489 083 21
XLYP	1.0000	1.524 451 61	0.091 806 33	5.365 665 90
B2PLYP	0.6400	1.039 911 46	0.429 170 78	4.645 905 70
DODBLYP	0.4700	1.212 975 12	0.401 529 93	4.290 436 57
DODPBEB95	0.5400	0.020 251 59	0.395 580 22	4.105 151 32
DODPBE	0.4800	0.815 040 08	0.389 470 68	4.408 172 49
DODPBEP86	0.5600	0.717 277 08	0.415 454 19	4.545 277 83
DODSVWN	0.4200	0.825 129 33	0.469 050 29	4.920 160 57
DSDBLYP	0.5400	0.605 205 04	0.462 677 88	4.765 928 88
DSDPBEB95	0.5400	-0.043 876 28	0.445 785 81	4.265 705 39
DSDPBE	0.4500	0.689 571 74	0.423 118 03	4.560 850 39
DSDPBEP86	0.4700	0.384 008 95	0.533 926 82	5.114 878 07
DSDSVWN	0.4100	0.505 482 01	0.493 429 33	4.923 045 17
MPW2PLYP	0.7500	0.540 937 06	0.485 556 73	4.897 993 20
PBE0-2	0.5000	0.084 871 84	0.672 636 08	5.706 371 26
PBE0-DH	0.8750	0.639 116 17	0.473 729 84	4.844 102 06
PWPB95	0.8200	-0.343 129 10	0.381 993 20	4.038 531 49

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
B1LYP	1.0000	1.828 803 61	0.385 011 63	4.455 947 54
B1P	1.0000	3.414 894 36	0.482 596 11	5.034 332 56
B3LYP	1.0000	1.937 944 71	0.404 216 83	4.456 882 14
B3P	1.0000	3.179 222 79	0.469 943 91	4.976 289 54
B3PW	1.0000	2.725 549 48	0.443 820 46	4.521 435 50
B97	1.0000	0.898 194 32	0.307 831 31	4.442 910 91
BHLYP	1.0000	1.510 231 86	0.282 349 67	5.289 492 64
BLYP	1.0000	2.088 032 66	0.417 359 56	4.040 648 05
BPBE	1.0000	3.547 654 67	0.493 935 34	4.196 033 29
BP	1.0000	3.116 535 07	0.410 014 65	4.909 639 55
BPW	1.0000	2.847 021 87	0.449 561 63	4.150 433 91
CAMB3LYP	1.0000	1.651 353 40	0.426 867 32	4.994 082 01
HF	1.0000	1.464 660 84	0.447 891 41	3.269 707 54
LB94	1.0000	2.189 197 93	0.341 839 80	3.373 283 49
LCBLYP	1.0000	1.678 421 02	0.647 893 74	7.026 901 36
M062X	1.0000	-0.046 517 39	0.864 406 44	7.335 741 36
M06	1.0000	0.537 337 69	0.588 132 71	5.972 627 95
M06L	1.0000	0.025 326 15	0.709 155 17	6.032 651 37
MPW1LYP	1.0000	1.338 318 37	0.299 692 13	5.170 758 67
MPW1PW	1.0000	1.632 824 99	0.415 464 43	4.599 968 98
MPWLYP	1.0000	1.365 297 71	0.286 929 36	4.909 775 14
MPWPW	1.0000	1.730 063 53	0.325 724 66	4.814 455 24
O3LYP	1.0000	1.738 609 49	0.106 394 57	6.050 070 81
OLYP	1.0000	2.464 503 35	0.555 166 17	2.598 730 72
OPBE	1.0000	2.693 574 00	0.612 873 20	2.357 318 16
PBE0	1.0000	1.197 310 44	0.417 719 77	4.883 923 53
PBE	1.0000	0.946 916 12	0.406 913 45	4.641 759 30
PW1PW	1.0000	1.182 413 29	0.469 534 06	4.882 870 74
PW6B95	1.0000	-0.155 125 37	0.082 305 24	5.939 151 72
PW86PBE	1.0000	1.466 136 03	0.426 463 95	4.671 057 25
PW91	1.0000	1.206 815 13	0.463 320 94	4.857 043 67
PWP1	1.0000	0.657 680 72	0.555 377 51	5.328 952 89
PWP	1.0000	0.594 888 96	0.476 895 43	5.643 999 80
REVPBE0	1.0000	1.499 517 83	0.358 443 24	4.161 581 45
REVPBE38	1.0000	1.797 885 36	0.387 728 41	4.459 850 24
REVPBE	1.0000	1.529 546 99	0.493 856 83	3.109 847 16
REVTPSS	1.0000	1.509 530 24	0.430 051 07	4.656 179 62
RPBE	1.0000	1.143 987 38	0.441 155 12	3.141 098 23
RPW86PBE	1.0000	1.238 725 11	0.398 202 83	4.694 258 39
SCAN	1.0000	0.471 019 79	0.615 727 66	5.899 556 34
TPSS0	1.0000	1.449 643 96	0.389 387 72	4.703 194 41
TPSS	1.0000	1.921 207 22	0.428 871 52	4.564 818 47
TPSSH	1.0000	2.162 249 73	0.451 934 99	4.652 948 62
WB97	1.0000	1.248 783 44	0.764 599 86	7.304 984 42
WB97X	1.0000	0.353 319 67	0.577 607 97	6.421 177 91

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
X3LYP	1.0000	1.505 108 76	0.211 721 84	5.478 182 74
XLYP	1.0000	1.509 740 73	0.090 561 28	5.362 356 65
B2PLYP	0.6400	1.012 167 54	0.416 439 20	4.631 809 80
DODBLYP	0.4700	1.088 350 02	0.375 699 17	4.239 898 63
DODPBEB95	0.5400	0.044 142 67	0.391 159 71	4.175 728 77
DODPBE	0.4800	0.812 157 20	0.382 440 55	4.378 137 88
DODPBEP86	0.5600	0.720 327 12	0.409 691 00	4.514 907 51
DODSVWN	0.4200	0.883 257 32	0.457 738 19	4.957 641 54
DSDBLYP	0.5400	0.626 825 76	0.454 540 10	4.729 579 26
DSDPBEB95	0.5400	−0.028 614 03	0.430 847 78	4.298 168 17
DSDPBE	0.4500	0.698 305 79	0.416 919 35	4.535 183 93
DSDPBEP86	0.4700	0.411 201 80	0.526 793 02	5.080 573 86
DSDSVWN	0.4100	0.736 010 01	0.501 012 70	5.064 186 73
MPW2PLYP	0.7500	0.556 673 24	0.480 979 71	4.879 449 49
PBE0-2	0.0500	0.267 800 51	0.679 862 98	5.761 994 48
PBE0-DH	0.8750	0.981 528 96	0.467 603 92	5.065 477 98
PWPB95	0.8200	−0.354 401 36	0.361 443 69	4.106 318 55

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. Extended statistical measures

As statistical measure for a set $\{x_1, \dots, x_n\}$ of data points with references $\{r_1, \dots, r_n\}$ we use

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

H. Statistical evaluation: S30L

Table A8: Extended 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 numeration of the systems regarding Ref. [19]

#	DLPNO- CCSD(T)/CBS*	PW6B95		SCAN		revPBE	
		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: Extended 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 numeration of the systems regarding Ref. [19]

#	DLPNO- CCSD(T)/CBS*	PW6B95		SCAN		revPBE	
		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: Extended 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 numeration of the systems regarding Ref. [19]

#	DLPNO- CCSD(T)/CBS*	PW6B95		SCAN		revPBE	
		D4	D3	D4	D3	D4	D3
1	-31.0	-30.2	-30.1	-29.1	-29.7	-32.5	-34.8
2	-20.7	-20.4	-20.4	-19.0	-19.4	-21.7	-23.1
3	-23.3	-21.0	-19.2	-21.8	-21.5	-23.6	-22.4
4	-18.6	-21.6	-20.3	-21.2	-21.0	-21.6	-20.2
5	-27.9	-33.6	-32.9	-32.1	-32.2	-34.8	-36.6
6	-25.2	-23.0	-22.8	-24.6	-25.2	-27.3	-29.5
7	-31.0	-33.6	-33.4	-32.0	-33.2	-37.0	-39.7
8	-35.6	-38.6	-38.7	-36.6	-38.0	-42.1	-45.6
9	-33.7	-33.9	-32.7	-30.8	-29.4	-38.4	-37.6
10	-35.0	-33.2	-32.0	-31.7	-30.2	-39.6	-39.0
11	-35.8	-37.5	-36.7	-36.5	-34.2	-48.0	-47.5
12	-36.9	-38.2	-37.5	-36.4	-34.1	-47.7	-47.4
13	-27.3	-27.4	-25.7	-26.5	-25.5	-26.2	-26.4
14	-28.6	-27.7	-26.7	-27.3	-26.6	-28.8	-29.2
15	-17.5	-18.3	-18.1	-21.6	-21.9	-21.4	-21.4
16	-21.6	-23.3	-23.9	-23.8	-24.2	-26.5	-26.6
17	-34.3	-33.0	-31.7	-35.5	-35.9	-33.0	-33.0
18	-22.8	-21.4	-20.4	-23.8	-24.0	-22.4	-22.2
19	-15.3	-15.8	-14.7	-16.6	-16.1	-14.7	-15.0
20	-18.5	-19.5	-17.9	-19.7	-19.1	-17.8	-18.1
21	-28.0	-28.0	-24.9	-27.0	-25.1	-29.1	-26.5
22	-35.3	-35.1	-33.9	-38.4	-38.8	-38.1	-36.4
23	-62.1	-62.5	-61.8	-66.3	-66.9	-67.0	-66.2
24	-136.3	-137.3	-133.1	-136.9	-134.7	-130.2	-128.4
25	-28.7	-30.8	-31.2	-28.9	-28.9	-31.0	-34.2
26	-28.6	-29.9	-30.3	-26.4	-26.5	-30.9	-34.1
27	-83.4	-83.3	-82.0	-84.0	-83.5	-79.8	-80.5
28	-80.0	-79.5	-78.7	-80.3	-80.1	-76.1	-77.3
29	-52.8	-56.1	-54.2	-58.2	-58.2	-55.7	-51.9
30	-49.6	-51.6	-49.9	-53.4	-53.4	-51.8	-48.5
MD		-0.7	0.3	-0.7	-0.4	-2.3	-2.5
MAD		1.5	1.8	1.9	2.3	3.5	3.9
RMSD		1.9	2.2	2.3	2.7	4.5	5.1
SD		9.7	11.7	12.2	14.8	21.4	24.4
Var		3.3	4.7	5.1	7.6	15.8	20.5
Max		2.3	4.1	3.3	4.8	6.1	7.9
Min		-5.7	-5.0	-5.4	-5.4	-12.2	-11.7
AMax		5.7	5.0	5.4	5.4	12.2	11.7

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 numeration of the systems regarding Ref. [22].

#	DLPNO- CCSD(T)/CBS*	PW6B95		PBE0		TPSS	
		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 numeration of the systems regarding Ref. [22].

#	DLPNO- CCSD(T)/CBS*	PW6B95		PBE0		TPSS	
		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 numeration of the systems regarding Ref. [22].

#	DLPNO- CCSD(T)/CBS*	PW6B95		PBE0		TPSS	
		D4	D3	D4	D3	D4	D3
CBH	-11.6	-9.4	-9.0	-12.0	-11.7	-12.0	-11.6
C2C2PD	-21.3	-20.3	-20.4	-20.0	-18.3	-22.9	-20.1
C3A	-17.0	-15.4	-14.9	-15.9	-14.4	-17.7	-15.3
C3GC	-29.1	-27.6	-26.6	-26.9	-24.2	-30.2	-25.9
GCGC	-12.8	-13.7	-12.4	-13.9	-12.1	-15.3	-12.5
GGG	-1.9	-1.9	-1.4	-2.1	-1.3	-2.8	-1.6
PHE	-23.0	-24.2	-23.7	-25.8	-25.3	-24.6	-23.9
MD		0.6	1.2	0.0	1.3	-1.3	0.8
MAD		1.2	1.4	1.3	2.0	1.3	1.1
RMSD		1.4	1.7	1.6	2.6	1.4	1.5
SD		3.2	3.1	4.1	5.8	1.8	3.3
Var		1.8	1.6	2.9	5.7	0.5	1.8
Max		2.2	2.6	2.2	4.9	-0.4	3.2
Min		-1.2	-0.7	-2.8	-2.3	-2.5	-0.9
AMax		2.2	2.6	2.8	4.9	2.5	3.2

J. Statistical evaluation: MOR41

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

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

#	Ref.	DOD-PBE			DSD-PBE		
		D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	-43.1	-46.2	-46.3	-47.4	-48.4	-48.4	-49.7
2	-46.6	-51.6	-51.8	-52.7	-54.2	-54.2	-55.4
3	-27.6	-35.8	-36.0	-36.6	-39.4	-39.4	-40.3
4	-62.5	-60.3	-60.5	-61.0	-58.5	-58.5	-59.4
5	3.7	2.9	2.7	2.3	3.7	3.7	3.0
6	-23.1	-21.7	-21.7	-20.4	-22.9	-22.9	-21.9
7	-16.2	-14.3	-14.2	-12.5	-14.8	-14.8	-13.3
8	-17.2	-13.5	-13.7	-13.4	-13.2	-13.2	-13.3
9	-18.8	-14.5	-14.6	-12.4	-14.2	-14.2	-13.2
10	-22.6	-21.9	-22.1	-23.2	-23.3	-23.3	-24.6
11	27.0	24.7	24.7	22.6	23.0	23.0	21.4
12	-29.8	-33.4	-33.5	-32.8	-35.5	-35.5	-35.2
13	-43.2	-45.8	-46.0	-47.1	-47.7	-47.7	-49.2
14	-52.0	-53.7	-54.0	-55.6	-55.1	-55.1	-56.7
15	-4.1	7.5	7.3	8.1	11.8	11.8	12.1
16	-39.8	-40.3	-40.8	-42.7	-40.3	-40.3	-41.7
17	-16.1	-13.9	-14.0	-11.2	-14.0	-14.0	-11.8
18	-34.2	-34.0	-34.4	-37.0	-33.7	-33.7	-36.2
19	-40.1	-39.9	-40.3	-43.0	-39.4	-39.4	-41.9
20	-30.2	-29.5	-29.8	-31.8	-28.8	-28.8	-30.9
21	-15.1	-17.2	-17.7	-18.6	-15.8	-15.8	-17.3
22	-35.9	-39.0	-39.4	-41.6	-40.3	-40.3	-42.6
23	-55.0	-55.1	-55.6	-58.9	-54.8	-54.8	-57.9
24	-41.6	-40.2	-41.1	-45.2	-39.9	-39.9	-42.7
25	-45.9	-45.2	-46.3	-50.5	-45.4	-45.4	-48.1
26	-36.4	-34.9	-35.2	-37.1	-33.3	-33.3	-34.7
27	-21.8	-21.1	-21.2	-22.7	-19.8	-19.8	-21.0
28	-36.3	-35.9	-36.1	-37.9	-34.6	-34.6	-36.0
29	-28.3	-28.7	-28.9	-30.3	-27.9	-27.9	-29.2
30	-14.9	-16.0	-16.2	-17.2	-14.9	-14.9	-15.8
31	-29.9	-29.4	-29.8	-31.2	-28.6	-28.6	-30.1
32	-1.9	-2.0	-2.0	-2.0	-2.3	-2.3	-2.1
33	-10.7	-6.7	-6.7	-5.8	-4.2	-4.2	-2.8
34	-25.6	-22.9	-23.0	-23.8	-21.0	-21.0	-21.3
35	-30.9	-28.3	-28.4	-29.9	-26.6	-26.6	-27.4
36	-39.8	-40.2	-40.4	-42.2	-40.0	-40.0	-41.1
37	-14.0	-16.9	-17.4	-17.4	-16.0	-16.0	-16.6
38	-64.4	-68.1	-68.6	-76.3	-67.4	-67.4	-74.0
39	-63.9	-63.3	-63.9	-65.8	-63.7	-63.7	-66.3
40	-65.8	-65.2	-65.4	-68.2	-64.9	-64.9	-67.7
41	-3.2	-2.4	-2.3	-1.4	-2.1	-2.1	-0.7
MD		0.1	-0.2	-1.3	0.2	0.2	-0.9
MAD		2.1	2.1	3.5	2.9	2.9	3.7
RMSD		3.1	3.1	4.4	4.3	4.3	5.0
SD		19.7	19.9	26.7	27.5	27.5	31.8
Var		9.7	9.9	17.8	18.9	18.9	25.3
Max		11.5	11.4	12.1	15.8	15.8	16.2
Min		-8.2	-8.4	-12.0	-11.8	-11.8	-12.7
AMax		11.5	11.4	12.1	15.8	15.8	16.2

Table A15: Extended statistical evaluations of : B3LYP and PBE0 in kcal mol⁻¹. We abbreviate D3(BJ)-ATM by D3.

#	Ref.	B3LYP			PBE0		
		D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	-43.1	-40.5	-40.6	-41.0	-44.6	-44.6	-44.7
2	-46.6	-41.9	-42.0	-42.3	-47.4	-47.4	-47.4
3	-27.6	-22.8	-22.9	-23.0	-26.4	-26.4	-26.4
4	-62.5	-66.2	-66.4	-66.5	-71.3	-71.3	-71.4
5	3.7	-0.1	-0.1	0.1	-2.6	-2.6	-2.4
6	-23.1	-17.4	-17.4	-15.9	-21.0	-21.0	-20.3
7	-16.2	-12.1	-12.0	-11.3	-15.7	-15.7	-15.3
8	-17.2	-12.8	-12.9	-11.8	-16.0	-16.0	-15.3
9	-18.8	-14.3	-14.3	-11.9	-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	28.2	30.9	30.9	30.2
12	-29.8	-24.6	-24.6	-22.8	-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	-43.6	-50.9	-50.9	-50.5
15	-4.1	-5.0	-5.1	-4.2	-4.8	-4.8	-4.4
16	-39.8	-39.3	-39.8	-39.7	-40.4	-40.4	-40.0
17	-16.1	-14.5	-14.6	-9.9	-13.7	-13.7	-11.2
18	-34.2	-31.8	-32.0	-31.7	-33.3	-33.3	-32.8
19	-40.1	-37.2	-37.4	-37.1	-38.7	-38.7	-38.0
20	-30.2	-29.2	-29.4	-28.6	-28.6	-28.6	-27.8
21	-15.1	-18.5	-18.8	-16.5	-18.7	-18.7	-17.1
22	-35.9	-32.3	-32.6	-30.6	-33.5	-33.5	-32.1
23	-55.0	-51.2	-51.4	-51.8	-52.6	-52.6	-52.3
24	-41.6	-40.8	-41.7	-42.9	-41.3	-41.3	-41.7
25	-45.9	-45.4	-46.4	-47.0	-45.6	-45.6	-45.6
26	-36.4	-42.4	-42.6	-43.6	-38.5	-38.5	-39.0
27	-21.8	-26.8	-27.0	-27.5	-25.1	-25.1	-25.5
28	-36.3	-41.7	-41.9	-42.5	-39.2	-39.2	-39.5
29	-28.3	-32.8	-33.0	-33.0	-30.0	-30.0	-30.0
30	-14.9	-21.8	-22.1	-21.6	-16.3	-16.3	-16.1
31	-29.9	-32.8	-33.2	-33.4	-29.4	-29.4	-29.7
32	-1.9	0.1	0.1	0.9	0.2	0.2	0.7
33	-10.7	-18.9	-19.0	-17.9	-9.4	-9.4	-8.8
34	-25.6	-30.3	-30.5	-30.5	-25.1	-25.1	-25.0
35	-30.9	-34.6	-34.7	-35.1	-29.8	-29.8	-29.9
36	-39.8	-39.4	-39.5	-40.9	-34.9	-34.9	-35.3
37	-14.0	-33.0	-33.4	-33.7	-23.3	-23.3	-23.4
38	-64.4	-72.2	-72.6	-78.5	-69.1	-69.1	-71.8
39	-63.9	-58.2	-58.5	-56.7	-60.7	-60.7	-59.5
40	-65.8	-66.4	-66.5	-67.2	-69.0	-69.0	-69.2
41	-3.2	-6.3	-6.3	-6.7	-3.0	-3.0	-3.4
MD		-0.1	-0.3	-0.2	-0.3	-0.3	0.0
MAD		4.2	4.2	4.8	2.3	2.3	2.6
RMSD		5.3	5.3	6.0	3.1	3.1	3.4
SD		33.7	33.9	38.3	19.7	19.7	21.8
Var		28.3	28.8	36.6	9.7	9.7	11.9
Max		8.2	7.9	8.4	5.0	5.0	4.9
Min		-19.0	-19.4	-19.6	-9.2	-9.2	-9.4
AMax		19.0	19.4	19.6	9.2	9.2	9.4

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

#	Ref.	PW6B95			CAM-B3LYP		
		D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	-43.1	-41.8	-41.8	-41.4	-40.1	-40.1	-40.1
2	-46.6	-42.9	-43.0	-42.5	-42.7	-42.7	-42.7
3	-27.6	-22.6	-22.6	-22.2	-23.2	-23.2	-23.1
4	-62.5	-63.0	-63.0	-62.4	-64.4	-64.4	-64.2
5	3.7	1.0	1.1	1.6	2.7	2.7	3.0
6	-23.1	-19.8	-19.7	-18.8	-19.5	-19.5	-18.6
7	-16.2	-16.5	-16.0	-15.0	-14.1	-14.1	-13.4
8	-17.2	-12.2	-12.4	-11.3	-15.8	-15.8	-14.8
9	-18.8	-12.5	-12.3	-10.0	-17.8	-17.8	-16.5
10	-22.6	-15.5	-15.6	-14.7	-15.8	-15.8	-15.3
11	27.0	32.8	33.0	32.3	33.6	33.6	33.1
12	-29.8	-28.4	-28.2	-26.7	-24.3	-24.3	-23.0
13	-43.2	-40.9	-40.7	-39.8	-38.4	-38.4	-37.9
14	-52.0	-47.9	-48.1	-47.4	-44.1	-44.1	-43.5
15	-4.1	-3.9	-4.0	-3.1	-9.6	-9.6	-9.1
16	-39.8	-40.0	-40.5	-39.7	-39.0	-39.0	-38.2
17	-16.1	-15.2	-15.2	-12.5	-16.2	-16.2	-13.1
18	-34.2	-29.4	-29.3	-30.9	-30.2	-30.2	-29.8
19	-40.1	-34.5	-34.5	-36.2	-36.4	-36.4	-35.9
20	-30.2	-27.1	-26.9	-26.7	-28.2	-28.2	-27.3
21	-15.1	-16.0	-16.1	-16.0	-14.4	-14.4	-12.8
22	-35.9	-26.1	-26.6	-29.3	-27.4	-27.4	-26.5
23	-55.0	-46.8	-46.7	-50.3	-49.0	-49.0	-49.2
24	-41.6	-39.7	-41.2	-42.0	-40.7	-40.7	-41.0
25	-45.9	-43.0	-44.7	-45.1	-45.0	-45.0	-44.7
26	-36.4	-33.5	-34.2	-35.6	-42.1	-42.1	-42.9
27	-21.8	-21.4	-22.1	-23.7	-27.4	-27.4	-28.2
28	-36.3	-34.3	-34.9	-36.6	-41.8	-41.8	-42.6
29	-28.3	-26.1	-26.7	-27.4	-32.1	-32.1	-32.4
30	-14.9	-9.9	-10.6	-11.6	-17.4	-17.4	-17.7
31	-29.9	-25.4	-26.4	-27.2	-33.3	-33.3	-34.1
32	-1.9	-1.2	-1.1	-1.5	0.5	0.5	0.8
33	-10.7	-10.5	-10.7	-10.7	-18.5	-18.5	-18.1
34	-25.6	-24.1	-24.4	-25.4	-28.6	-28.6	-28.8
35	-30.9	-28.7	-29.0	-31.0	-32.7	-32.7	-33.3
36	-39.8	-33.5	-33.5	-37.2	-36.5	-36.5	-37.7
37	-14.0	-19.6	-20.2	-19.3	-26.7	-26.7	-26.9
38	-64.4	-59.6	-60.5	-64.0	-67.0	-67.0	-70.0
39	-63.9	-61.0	-61.2	-60.5	-60.8	-60.8	-59.8
40	-65.8	-66.2	-66.2	-66.9	-65.9	-65.9	-66.2
41	-3.2	-1.0	-1.4	-2.2	-5.9	-5.9	-6.6
MD		2.7	2.4	2.1	0.5	0.5	0.7
MAD		3.2	3.0	2.7	3.7	3.7	4.3
RMSD		4.0	3.8	3.5	4.6	4.6	5.0
SD		18.9	19.1	18.0	28.9	28.9	31.4
Var		8.9	9.1	8.1	21.0	21.0	24.7
Max		9.8	9.2	8.7	8.5	8.5	9.3
Min		-5.6	-6.2	-5.3	-12.7	-12.7	-12.8
AMax		9.8	9.2	8.7	12.7	12.7	12.8

Table A17: Extended statistical evaluations of : revPBE and M06L in kcal mol⁻¹. We abbreviate D3(BJ)-ATM by D3.

#	Ref.	revPBE			M06L		
		D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	-43.1	-44.5	-44.6	-44.1	-41.0	-41.0	-40.7
2	-46.6	-47.6	-47.6	-47.0	-45.1	-45.1	-44.9
3	-27.6	-29.0	-29.1	-28.4	-27.1	-27.1	-26.9
4	-62.5	-73.6	-73.8	-72.4	-64.9	-64.9	-64.7
5	3.7	-6.8	-6.7	-5.4	-2.7	-2.7	-2.5
6	-23.1	-17.9	-17.9	-15.5	-18.1	-18.1	-18.1
7	-16.2	-12.9	-12.9	-11.3	-16.8	-16.8	-16.8
8	-17.2	-14.2	-14.3	-12.3	-7.7	-7.7	-7.5
9	-18.8	-14.0	-13.8	-9.7	-7.2	-7.2	-8.2
10	-22.6	-24.6	-24.7	-23.3	-13.2	-13.2	-12.7
11	27.0	24.2	24.5	22.7	30.7	30.7	31.3
12	-29.8	-30.6	-30.4	-26.8	-24.7	-24.7	-24.3
13	-43.2	-44.8	-44.7	-42.9	-39.8	-39.8	-39.4
14	-52.0	-51.2	-51.3	-49.5	-50.0	-50.0	-49.2
15	-4.1	1.9	1.7	4.0	5.4	5.4	5.5
16	-39.8	-41.7	-42.0	-40.4	-42.3	-42.3	-40.6
17	-16.1	-14.8	-14.9	-7.8	-18.2	-18.2	-17.7
18	-34.2	-34.8	-34.5	-32.9	-24.7	-24.7	-23.9
19	-40.1	-39.0	-38.5	-37.2	-28.8	-28.8	-27.7
20	-30.2	-31.2	-30.9	-28.7	-24.6	-24.6	-23.6
21	-15.1	-23.9	-23.7	-18.9	-13.7	-13.7	-12.7
22	-35.9	-37.5	-37.1	-35.2	-21.8	-21.8	-20.7
23	-55.0	-52.2	-51.6	-51.5	-40.8	-40.8	-39.8
24	-41.6	-39.1	-40.0	-41.1	-39.0	-39.0	-36.8
25	-45.9	-43.5	-44.7	-45.4	-44.0	-44.0	-41.1
26	-36.4	-35.5	-35.6	-37.6	-33.7	-33.7	-33.0
27	-21.8	-21.5	-21.7	-24.1	-22.2	-22.2	-22.1
28	-36.3	-36.0	-36.2	-38.1	-33.9	-33.9	-33.5
29	-28.3	-28.9	-29.1	-29.7	-25.7	-25.7	-25.4
30	-14.9	-23.2	-23.2	-23.6	-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	0.0	1.4	1.4	1.4
33	-10.7	-10.5	-10.6	-10.0	-12.1	-12.1	-11.8
34	-25.6	-25.1	-25.1	-25.9	-22.1	-22.1	-21.7
35	-30.9	-29.1	-29.0	-30.3	-23.6	-23.6	-23.2
36	-39.8	-33.6	-33.2	-36.0	-29.8	-29.8	-29.6
37	-14.0	-29.7	-30.4	-28.1	-26.4	-26.4	-26.1
38	-64.4	-73.0	-73.0	-78.5	-59.1	-59.1	-57.4
39	-63.9	-56.7	-56.8	-52.8	-56.1	-56.1	-55.6
40	-65.8	-66.7	-66.5	-66.4	-65.0	-65.0	-64.7
41	-3.2	-1.3	-1.4	-4.3	-4.7	-4.7	-4.9
MD		-0.6	-0.6	0.1	3.6	3.6	4.2
MAD		3.3	3.3	3.8	5.1	5.1	5.4
RMSD		4.8	4.9	5.4	6.4	6.4	6.8
SD		30.7	31.0	34.8	34.1	34.1	34.5
Var		23.6	24.1	30.3	29.1	29.1	29.7
Max		7.2	7.2	11.1	14.2	14.2	15.2
Min		-15.7	-16.3	-14.2	-12.4	-12.4	-12.1
AMax		15.7	16.3	14.2	14.2	14.2	15.2

Table A18: Extended statistical evaluations of : PBE and RPBE in kcal mol⁻¹. We abbreviate D3(BJ)-ATM by D3.

#	Ref.	PBE			RPBE		
		D4-ATM	D4-MBD	D3	D4-ATM	D4-MBD	D3
1	-43.1	-46.7	-46.8	-46.6	-44.4	-44.4	-49.0
2	-46.6	-50.0	-50.0	-49.9	-47.3	-47.3	-51.6
3	-27.6	-31.5	-31.5	-31.3	-28.8	-28.8	-31.8
4	-62.5	-75.1	-75.2	-75.0	-74.0	-74.0	-76.4
5	3.7	-7.4	-7.4	-7.0	-7.2	-7.2	-8.6
6	-23.1	-20.4	-20.4	-19.6	-17.7	-17.7	-11.6
7	-16.2	-14.9	-14.8	-14.7	-12.1	-12.1	-4.3
8	-17.2	-14.4	-14.5	-13.7	-14.1	-14.1	-13.6
9	-18.8	-16.0	-15.9	-15.0	-15.3	-15.3	-10.5
10	-22.6	-24.5	-24.6	-23.9	-24.6	-24.6	-28.1
11	27.0	25.0	25.0	24.6	24.4	24.4	18.2
12	-29.8	-30.8	-30.7	-29.4	-30.8	-30.8	-26.0
13	-43.2	-45.2	-45.2	-44.7	-44.9	-44.9	-48.9
14	-52.0	-52.3	-52.5	-51.4	-51.2	-51.2	-55.5
15	-4.1	1.2	1.1	1.7	1.2	1.2	3.8
16	-39.8	-39.5	-39.9	-38.5	-40.5	-40.5	-42.2
17	-16.1	-14.4	-14.5	-11.7	-14.6	-14.6	-2.1
18	-34.2	-32.5	-32.6	-31.0	-36.0	-36.0	-44.7
19	-40.1	-36.3	-36.4	-34.6	-39.9	-39.9	-48.6
20	-30.2	-28.1	-28.1	-26.5	-32.2	-32.2	-38.0
21	-15.1	-20.4	-20.6	-18.0	-25.2	-25.2	-28.0
22	-35.9	-35.2	-35.4	-32.5	-38.5	-38.5	-48.8
23	-55.0	-50.2	-50.3	-48.5	-53.8	-53.8	-65.6
24	-41.6	-36.8	-37.6	-36.3	-38.1	-38.1	-47.5
25	-45.9	-41.4	-42.3	-40.4	-41.6	-41.6	-50.6
26	-36.4	-34.9	-35.1	-34.9	-35.6	-35.6	-41.8
27	-21.8	-21.9	-22.1	-22.0	-21.8	-21.8	-30.1
28	-36.3	-35.5	-35.7	-35.4	-36.3	-36.3	-44.2
29	-28.3	-27.7	-27.8	-27.4	-29.0	-29.0	-35.5
30	-14.9	-19.9	-20.1	-19.2	-23.6	-23.6	-28.7
31	-29.9	-26.6	-26.9	-26.6	-28.9	-28.9	-36.5
32	-1.9	0.9	0.9	1.5	-0.5	-0.5	-0.4
33	-10.7	-9.5	-9.6	-8.8	-10.1	-10.1	-5.2
34	-25.6	-23.8	-23.9	-23.3	-25.0	-25.0	-27.0
35	-30.9	-28.1	-28.2	-27.6	-29.2	-29.2	-34.1
36	-39.8	-32.8	-32.9	-32.8	-34.3	-34.3	-41.5
37	-14.0	-29.8	-30.0	-29.8	-30.3	-30.3	-31.1
38	-64.4	-68.5	-68.8	-70.0	-73.9	-73.9	-99.4
39	-63.9	-57.0	-57.2	-55.1	-58.6	-58.6	-68.8
40	-65.8	-68.4	-68.5	-68.1	-67.4	-67.4	-79.4
41	-3.2	-2.8	-2.9	-3.6	-1.1	-1.1	2.6
MD		-0.1	-0.3	0.5	-0.9	-0.9	-4.7
MAD		3.5	3.4	3.9	3.4	3.4	8.3
RMSD		4.8	4.7	5.1	5.0	5.0	10.1
SD		30.5	30.4	32.4	31.4	31.4	57.5
Var		23.3	23.0	26.3	24.6	24.6	82.6
Max		7.0	6.9	8.8	5.5	5.5	14.0
Min		-15.7	-16.0	-15.8	-16.2	-16.2	-35.0
AMax		15.7	16.0	15.8	16.2	16.2	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.

#	Ref.	DSDBLYP		B3LYP		PW6B95		PBE	
		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.

#	Ref.	DSDBLYP		B3LYP		PW6B95		PBE		
		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.

#	Ref.	DSDBLYP		B3LYP		PW6B95		PBE	
		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.

#	Ref.	DSDBLYP		B3LYP		PW6B95		PBE	
		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.

#	rot. const	Ref.	PBE0		PBE		TPSS	
			D3	D4	D3	D4	D3	D4
1	A	4293.9	4299.8	4298.1	4240.8	4238.8	4235.9	4235.8
	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
2	A	3322.5	3309.3	3307.7	3247.0	3247.8	3239.0	3240.4
	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
3	A	3071.1	3071.9	3071.3	3023.0	3022.8	3021.0	3022.3
	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
4	A	2755.9	2765.6	2765.8	2731.3	2731.7	2729.3	2730.3
	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
7	A	1165.7	1170.2	1170.4	1152.1	1153.5	1154.6	1155.9
	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
8	A	1166.3	1167.7	1168.3	1147.9	1148.4	1153.1	1155.3
	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
9	A	862.5	865.9	866.0	852.4	852.4	853.2	853.8
	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
10	A	3086.2	3101.0	3100.5	3060.2	3059.9	3061.3	3061.6
	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
11	A	1432.1	1436.0	1435.5	1416.5	1416.5	1418.6	1418.9
	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
12	A	1523.2	1523.3	1521.2	1496.3	1495.8	1497.2	1497.4
	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.

#	rot. const	Ref.	PBE0		PBE		TPSS	
			D3	D4	D3	D4	D3	D4
1	A	4293.9	4299.8	4300.5	4240.8	4239.3	4235.9	4239.0
	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
2	A	3322.5	3309.3	3308.4	3247.0	3247.9	3239.0	3243.4
	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
3	A	3071.1	3071.9	3072.6	3023.0	3023.1	3021.0	3024.1
	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
4	A	2755.9	2765.6	2766.1	2731.3	2732.3	2729.3	2732.0
	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
6	A	1464.2	1471.0	1471.4	1440.0	1440.2	1439.1	1440.7
	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
7	A	1165.7	1170.2	1170.1	1152.1	1153.4	1154.6	1156.2
	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
8	A	1166.3	1167.7	1168.3	1147.9	1149.6	1153.1	1158.8
	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
9	A	862.5	865.9	866.0	852.4	852.6	853.2	854.7
	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
10	A	3086.2	3101.0	3100.8	3060.2	3060.5	3061.3	3063.5
	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
11	A	1432.1	1436.0	1435.6	1416.5	1416.4	1418.6	1421.2
	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
12	A	1523.2	1523.3	1520.1	1496.3	1495.5	1497.2	1499.0
	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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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 ₂ O(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 ₂ H 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 ₂ H 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 ₂ O(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 ₂ H ₂ (C-C)	120.3	119.6	119.6	120.6	120.6	120.2	120.2
CH ₂ O(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 ₂ H 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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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 ₂ O(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 ₂ H 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 ₂ H 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 ₂ O(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 ₂ H ₂ (C-C)	120.3	119.6	119.6	120.6	120.2	120.2	120.2
CH ₂ O(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 ₂ H 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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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 ₂ H 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 ₂ H ₂ (Se-Se)	234.6	232.4	232.4	235.0	235.0	234.4	234.4
Ge ₂ H 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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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 ₂ H 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 ₂ H ₂ (Se-Se)	234.6	232.4	232.4	235.0	235.0	234.4	234.5
Ge ₂ H 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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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) ₂ Cl ₂ (Ti–C)	205.8	203.5	203.6	205.5	205.5	206.3	206.3
Ti(CH ₃) ₂ Cl 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 ₂ F ₂ (Cr=O)	157.4	153.7	153.6	157.1	157.1	157.0	157.0
CrO ₂ F ₂ (Cr–F)	171.9	170.2	170.2	172.4	172.3	172.0	172.0
CrO ₂ Cl ₂ (Cr=O)	157.7	153.8	153.8	157.2	157.2	157.2	157.1
CrO ₂ Cl 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 ₆ H ₆) ₂ (Cr–C)	215.0	213.0	212.9	213.8	213.7	213.6	213.5
Cr(C ₆ H ₆)(CO) ₃ (Cr–C ^{Ar})	220.8	219.1	219.2	221.0	221.1	220.2	220.2
Cr(C ₆ H 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 ₃ F(Mn=O)	158.6	154.2	154.2	159.2	157.7	157.6	157.6
MnO ₃ F(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 ^{CH₂})	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 ₂ H ₄)(CO) ₄ (Fe–C ^{et})	211.7	209.7	216.2	213.0	216.7	212.3	216.7
Fe(C ₂ H ₄)(CO) ₄ (Fe–C ^{ax})	181.5	180.0	180.1	179.9	179.9	180.7	180.7
Fe(C ₂ H 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.

system(bond)	Ref.	PBE0		PBE		TPSS	
		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) ₂ Cl ₂ (Ti–C)	205.8	203.5	203.6	205.5	205.5	206.3	206.4
Ti(CH ₃) ₂ Cl 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 ₂ F ₂ (Cr=O)	157.4	153.7	153.7	157.1	157.1	157.0	157.0
CrO ₂ F ₂ (Cr–F)	171.9	170.2	170.2	172.4	172.4	172.0	172.0
CrO ₂ Cl ₂ (Cr=O)	157.7	153.8	153.8	157.2	157.2	157.2	157.2
CrO ₂ Cl 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 ₆ H ₆) ₂ (Cr–C)	215.0	213.0	213.0	213.8	213.7	213.6	213.6
Cr(C ₆ H ₆)(CO) ₃ (Cr–C ^{Ar})	220.8	219.1	219.2	221.0	221.1	220.2	220.3
Cr(C ₆ H 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 ₃ F(Mn=O)	158.6	154.2	154.2	159.2	157.7	157.6	157.6
MnO ₃ F(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 ^{CH₂})	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 ₂ H ₄)(CO) ₄ (Fe–C ^{et})	211.7	209.7	209.9	213.0	213.1	212.3	212.6
Fe(C ₂ H ₄)(CO) ₄ (Fe–C ^{ax})	181.5	180.0	180.0	179.9	179.9	180.7	180.7
Fe(C ₂ H 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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