Electronic Supporting Information

What types of chemical problems benefit from density-corrected DFT? A probe using an extensive and chemically diverse test suite

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Table S1: Abbreviations used and their descriptions

Abbreviation	Description
ACONF[1]	Relative energies of alkane conformers
ADIM6[2]	Interaction energies of n-alkane dimers
AHB21[3]	Interaction energies in anion–neutral dimers
AL2X6[4]	Dimerisation energies of AlX3 compounds
ALK8[4]	Dissociation and other reactions of alkaline compounds
ALKBDE10[5]	Dissociation energies in group-1 and -2 diatomics
AMINO20X4[6]	Relative energies in amino acid conformers
BH76RC[7]	Barrier heights of hydrogen transfer, heavy atom transfer, nucleophilic substitution, unimolecular and association reactions
BH76[8,9,7]	Reaction energies of the BH7610,11,23 set
BHDIV10[4]	Diverse reaction barrier heights
BHPERI[4,10,11,12]	Barrier heights of pericyclic reactions
BHROT27[4]	Barrier heights for rotation around single bonds
BSR36[13,14]	Bond-separation reactions of saturated hydrocarbons
BUT14DIOL[15]	Relative energies in butane-1,4-diol conformers
C60ISO[16]	Relative energies between C60 isomers
CARBHB12[4]	Hydrogen-bonded complexes between carbene analogues and H2O, NH3, or HCl
CDIE20[17]	Double-bond isomerisation energies in cyclic systems
CHB6[3]	Interaction energies in cation–neutral dimers
DARC[7,18]	Reaction energies of Diels–Alder reactions
DC13[19,7,20,21–29]	13 difficult cases for DFT methods
DIPCS10[4]	Double-ionisation potentials of closed-shell systems
FH51[30,31]	Reaction energies in various (in-)organic systems
G21EA[7,32]	Adiabatic electron affinities
G21IP[7,32]	Adiabatic ionisation potentials
G2RC[7,33]	Reaction energies of selected G2/97 systems
HAL59[34,35]	Binding energies in halogenated dimers (incl. halogen bonds)
HEAVY28[9]	Noncovalent interaction energies between heavy element hydrides
HEAVYSB11[4]	Dissociation energies in heavy-element compounds
ICONF[4]	Relative energies in conformers of inorganic systems
IDISP[7,36–39]	Intramolecular dispersion interactions
IL16[3]	Interaction energies in anion–cation dimers
INV24[40]	Inversion/racemisation barrier heights
ISO34[36]	Isomerisation energies of small and medium-sized organic molecules
ISOL24[41]	Isomerisation energies of large organic molecules
MB16-43[4]	Decomposition energies of artificial molecules
MCONF[42]	Relative energies in melatonin conformers
NBPRC[7,38,43]	Oligomerisations and H2 fragmentations of NH3/BH3 systems;H2 activation reactions with PH3/BH3 systems
PA26[4]	Adiabatic proton affinities (incl. of amino acids)
PArel[4]	Relative energies in protonated isomers
PCONF21	Relative energies in tri- and tetrapeptide conformers
PNICO23[44]	Interaction energies in pnicogen-containing dimers
PX13[45]	Proton-exchange barriers in H2O, NH3, and HF clusters
RC21[4]	Fragmentations and rearrangements in radical cations
RG18[4]	Interaction energies in rare-gas complexes

RSE43[46]	Radical-stabilisation energies
S22[47]	Binding energies of noncovalently bound dimers
S66[48]	Binding energies of noncovalently bound dimers
SCONF[7,49]	Relative energies of sugar conformers
SIE4X4[50]	Self-interaction-error related problems
TAUT15[4]	Relative energies in tautomers
UPU23[51]	Relative energies between RNA-backbone conformers
W4-11[52]	Total atomisation energies
WATER27[53]	Binding energies in (H2O)n, H+(H2O)n and OH−(H2O)n
WCPT18[54]	Proton-transfer barriers in uncatalysed and water-catalysed reactions
YBDE18[55]	Bond-dissociation energies in ylides

Table S2: Original and Optimized D4 parameters for HF-DFT and self-consistent DFT functionals together with five major subcategories of total WTMAD2

Functionals	s_6	a_1	s_8	a_2	Five top level subsets					WTMAD2
					THERMO[a]	BARRIERS[b]	LARGE[c]	CONF[d]	INTERMOL[e]	
HF-PBE-D4	1.0	0.5586	1.1145	3.6542	1.473	1.372	1.454	1.074	0.900	6.273
HF-PBE0-D4	1.0	0.4909	1.0402	4.2328	1.232	0.843	1.227	0.927	0.786	5.014
HF-PBE38-D4	1.0	0.4560	1.0815	4.5749	1.483	0.758	1.315	0.959	0.838	5.353
HF-PBE50-D4	1.0	0.4042	0.7455	4.7098	1.717	0.831	1.486	0.997	0.985	6.016
HF-BLYP-D4	1.0	0.4826	1.7143	3.2824	1.528	1.121	1.569	1.225	1.110	6.553
HF-B20LYP-D4	1.0	0.4215	1.2898	3.6437	1.351	0.663	1.222	0.994	0.869	5.100
HF-B3LYP-D4	1.0	0.4196	1.2556	3.7554	1.146	0.675	1.208	0.949	0.827	4.804
HF-B1LYP-D4	1.0	0.4102	1.1892	3.7353	1.279	0.600	1.188	0.939	0.835	4.840
HF-B38LYP-D4	1.0	0.3754	0.8643	3.8684	1.368	0.613	1.078	0.893	0.907	4.860
HF-BHLYP-D4	1.0	0.3624	0.6822	3.9886	1.563	0.879	1.069	0.988	1.000	5.499
HF-TPSS-D4	1.0	0.3303	1.3673	4.5177	1.424	0.891	1.566	0.853	0.975	5.709
HF-TPSSh-D4	1.0	0.5162	1.4287	3.7716	1.375	1.015	1.362	0.841	0.848	5.441
HF-TPSS0-D4	1.0	0.4743	1.2502	4.0521	1.449	0.817	1.214	0.755	0.859	5.094
HF-TPSS38-D4	1.0	0.4198	0.7804	4.1058	1.605	0.811	1.260	0.767	0.938	5.381
HF-TPSS50-D4	1.0	0.3928	0.7222	4.3802	1.894	0.932	1.387	0.885	1.027	6.125
HF-SCAN-D4	1.0	0.1586	0.7155	7.4456	1.303	1.045	1.075	0.900	0.757	5.079
HF-SCAN10-D4	1.0	0.2161	1.0159	7.3021	1.334	0.898	1.059	0.905	0.764	4.960
HF-SCAN0-D4	1.0	0.2290	1.0482	7.2144	1.509	0.786	1.141	0.949	0.787	5.172
HF-SCAN38-D4	1.0	0.2493	0.8788	6.9488	1.702	0.767	1.254	1.008	0.849	5.579
HF-SCAN50-D4	1.0	0.2810	0.5959	6.4527	1.947	0.849	1.374	1.067	0.943	6.181
HF-mPW1K-D4	1.0	1.1270	0.4163	4.4405	1.595	0.771	1.252	0.926	1.024	5.569
PBE-D4	1.0	0.7233	4.7411	4.7199	2.052	2.319	2.114	1.812	1.618	9.914
PBE-D4orig[1]	1.0	0.3857	0.9595	4.8069	2.078	2.407	1.946	1.879	2.117	10.426

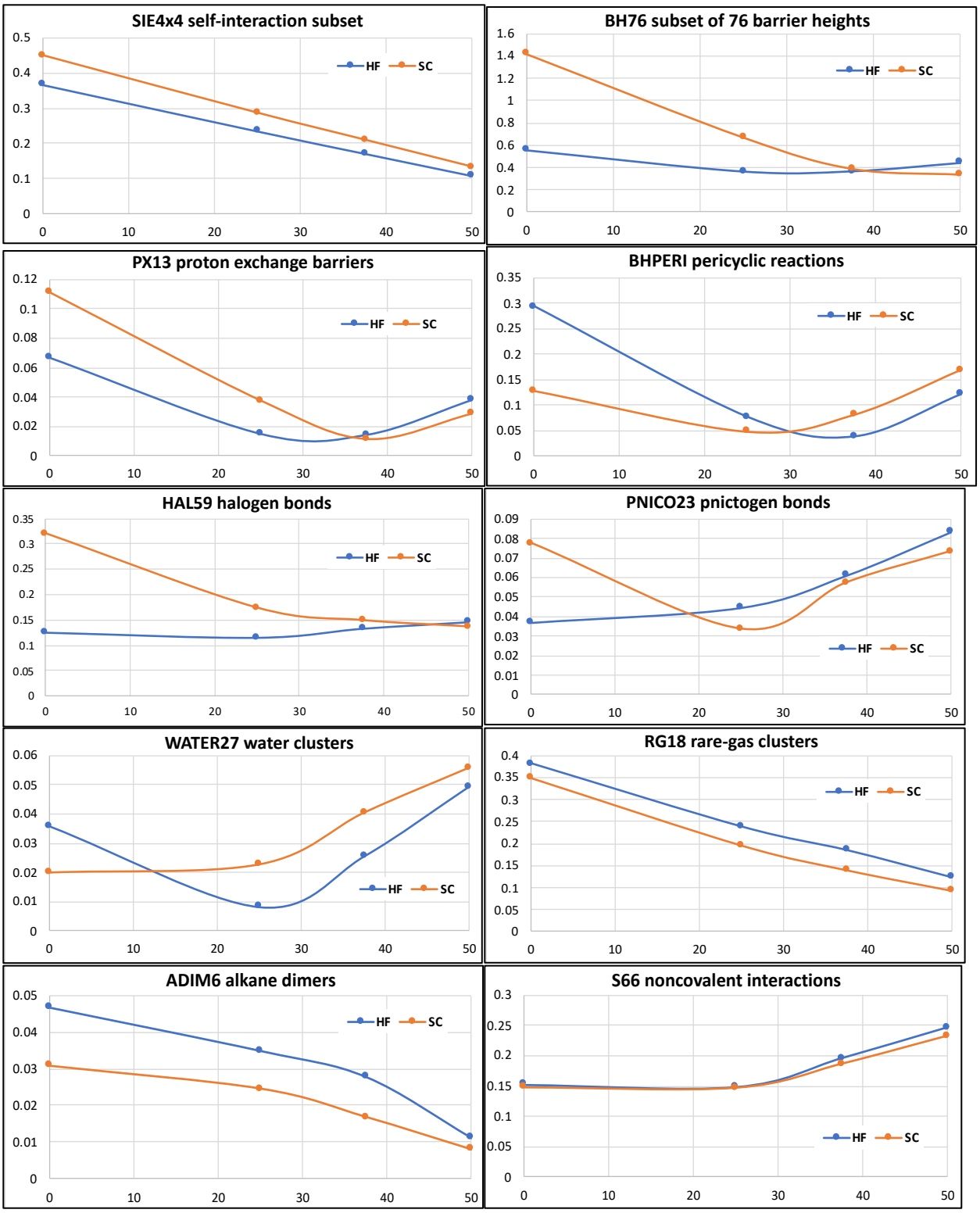
[1] All "original" parameters are taken from ref[56,57].

PBE0-D4	1.0	0.5835	4.3194	5.3549	1.336	1.144	1.412	1.245	1.065	6.202
PBE0-D4orig[1]	1.0	0.4009	1.2007	5.0293	1.361	1.204	1.342	1.245	1.267	6.418
PBE38-D4	1.0	0.5208	2.8361	5.2438	1.482	0.762	1.331	1.098	0.981	5.653
PBE50-D4	1.0	0.4424	1.9249	5.3064	1.714	0.641	1.395	1.074	1.024	5.848
BLYP-D4	1.0	0.4702	3.6496	4.6263	2.062	1.931	2.461	1.629	1.282	9.365
BLYP-D4orig[1]	1.0	0.4449	2.3408	4.0933	2.006	2.066	2.188	1.851	1.493	9.603
B20LYP-D4	1.0	0.4355	2.1734	4.4258	1.4345	1.0656	1.7045	1.1361	0.9017	6.242
B3LYP-D4	1.0	0.4635	2.5224	4.5658	1.327	1.099	1.722	1.202	0.911	6.261
B3LYP-D4orig[1]	1.0	0.4087	2.0293	4.5381	1.301	1.124	1.610	1.235	1.096	6.366
B1LYP-D4	1.0	0.4296	1.8888	4.3733	1.376	0.900	1.548	1.045	0.849	5.717
B1LYP-D4orig[1]	1.0	0.3931	1.9855	4.5547	1.360	0.898	1.505	1.083	0.949	5.794
B38LYP-D4	1.0	0.3999	1.2738	4.2818	1.405	0.660	1.202	0.950	0.873	5.090
BHLYP-D4	1.0	0.3665	0.9499	4.4188	1.579	0.791	1.073	1.005	0.926	5.374
BHLYP-D4orig[1]	1.0	0.2726	1.6528	5.4863	1.601	0.839	1.192	1.074	0.940	5.646
TPSS-D4	1.0	0.5886	5.4374	5.0607	1.912	2.064	2.111	1.524	1.265	8.876
TPSS-D4orig[1]	1.0	0.4282	1.7660	4.5426	1.819	2.177	1.862	1.726	1.629	9.213
TPSSh-D4	1.0	0.5634	4.4400	4.9713	2.068	1.616	1.748	1.267	1.110	7.809
TPSSh-D4orig[1]	1.0	0.4429	1.8590	4.6023	1.577	1.694	1.593	1.391	1.307	7.562
TPSS0-D4	1.0	0.5050	3.3687	5.0625	1.496	1.045	1.340	0.992	0.969	5.842
TPSS0-D4orig[1]	1.0	0.4033	1.6244	4.8054	1.504	1.103	1.246	1.054	1.102	6.008
TPSS38-D4	1.0	0.4652	2.6661	5.1069	1.613	0.764	1.244	0.916	0.939	5.477
TPSS50-D4	1.0	0.4144	1.6981	5.0215	1.858	0.808	1.304	0.917	1.001	5.887
SCAN-D4	1.0	0.1898	3.0789	9.0102	2.330	1.895	1.360	1.226	1.594	8.404
SCAN-D4orig[1]	1.0	0.6293	1.4613	6.3128	2.331	1.898	1.347	1.237	1.708	8.521
SCAN10-D4	1.0	0.3149	6.4925	8.7697	1.531	1.510	1.228	1.105	1.419	6.793
SCAN0-D4	1.0	0.3750	6.1187	8.1124	1.549	1.040	1.192	1.001	1.198	5.980
SCAN38-D4	1.0	0.3996	5.0438	7.6249	1.691	0.768	1.256	0.997	1.075	5.788
SCAN50-D4	1.0	0.4108	3.2856	6.9783	1.901	0.754	1.377	1.055	1.051	6.138
mPW1K-D4	1.0	2.6336	0.4574	5.1437	1.506	0.603	1.220	1.042	1.038	5.409

[a]THERMO=Small Molecule Thermochemistry; [b]BARRIER=barrier heights; [c]LARGE=reaction energies for large systems; [d]CONF=conformer/intramolecular interactions; and [e]INTERMOL=intermolecular interactions

Table S3: Dispersion free HF-DFT and SC-DFT functionals together with five major subcategories of total WTMAD2

Functionals	Five top level subsets					WTMAD2
	THERMO	BARRIERS	LARGE	CONF	INTERMOL	
HF-PBE	1.570	1.132	2.316	4.601	4.222	13.840
HF-PBE0	1.246	0.698	1.821	4.048	3.885	11.697
HF-PBE38	1.458	0.706	1.730	3.802	3.704	11.400
HF-PBE50	1.671	0.875	1.786	3.575	3.580	11.487
HF-BLYP	2.212	0.907	3.429	6.676	8.807	22.030
HF-B20LYP	1.952	0.814	2.855	5.730	7.258	18.610
HF-B3LYP	1.660	0.784	2.719	5.485	6.800	17.446
HF-B1LYP	1.822	0.838	2.714	5.478	6.847	17.699
HF-B38LYP	1.784	1.023	2.426	4.956	5.942	16.131
HF-BHLYP	1.827	1.273	2.218	4.428	5.027	14.773
HF-TPSS	1.672	0.910	2.712	5.232	5.710	16.235
HF-TPSSh	1.555	0.750	2.440	4.941	5.410	15.095
HF-TPSS0	1.518	0.714	2.086	4.546	5.022	13.886
HF-TPSS38	1.608	0.849	1.933	4.241	4.713	13.345
HF-TPSS50	1.843	1.088	1.874	3.961	4.413	13.179
HF-SCAN	1.294	0.988	1.283	1.880	2.026	7.472
HF-SCAN10	1.331	0.846	1.252	1.930	2.019	7.377
HF-SCAN0	1.496	0.739	1.304	2.041	2.060	7.640
HF-SCAN38	1.683	0.738	1.403	2.153	2.116	8.092
HF-SCAN50	1.920	0.859	1.529	2.273	2.192	8.774
HF-mPW1K	1.577	0.819	1.777	4.286	4.845	13.304
PBE	2.083	2.194	2.640	3.817	3.157	13.891
PBE0	1.348	1.044	1.886	3.477	3.151	10.905
PBE38	1.466	0.692	1.720	3.389	3.217	10.484
PBE50	1.660	0.674	1.722	3.324	3.335	10.715
BLYP	2.373	1.904	3.732	5.707	7.141	20.857
B20LYP	1.777	1.129	2.949	5.120	6.215	17.190
B3LYP	1.586	1.151	2.823	4.810	5.635	16.005
B1LYP	1.709	0.989	2.766	4.938	5.927	16.328
B38LYP	1.694	0.857	2.386	4.584	5.304	14.824
BHLYP	1.776	1.036	2.112	4.193	4.634	13.751
TPSS	1.934	1.898	2.894	4.374	4.537	15.636
TPSSh	1.683	1.465	2.545	4.206	4.443	14.342
TPSS0	1.563	0.973	2.093	4.014	4.377	13.020
TPSS38	1.632	0.786	1.872	3.885	4.316	12.491
TPSS50	1.829	0.937	1.780	3.768	4.245	12.558
SCAN	2.308	1.865	1.481	1.576	2.169	9.400
SCAN10	1.522	1.476	1.357	1.598	2.098	8.051
SCAN0	1.540	0.995	1.322	1.668	2.020	7.545
SCAN38	1.672	0.734	1.391	1.815	2.048	7.660
SCAN50	1.875	0.762	1.516	2.030	2.134	8.316
mPW1K	1.497	0.617	1.722	3.951	4.447	12.234


SIE4x4 self-interaction subset
HF
SC
BH76 subset of 76 barrier heights
HF
SC
PX13 proton exchange barriers
HF
SC
BHPERI pericyclic reactions
HF
SC
HAL59 halogen bonds
HF
SC
PNICO23 pnictogen bonds
HF
SC
WATER27 water clusters
HF
SC
RG18 rare-gas clusters
HF
SC
ADIM6 alkane dimers
HF
SC
S66 noncovalent interactions
HF
SC

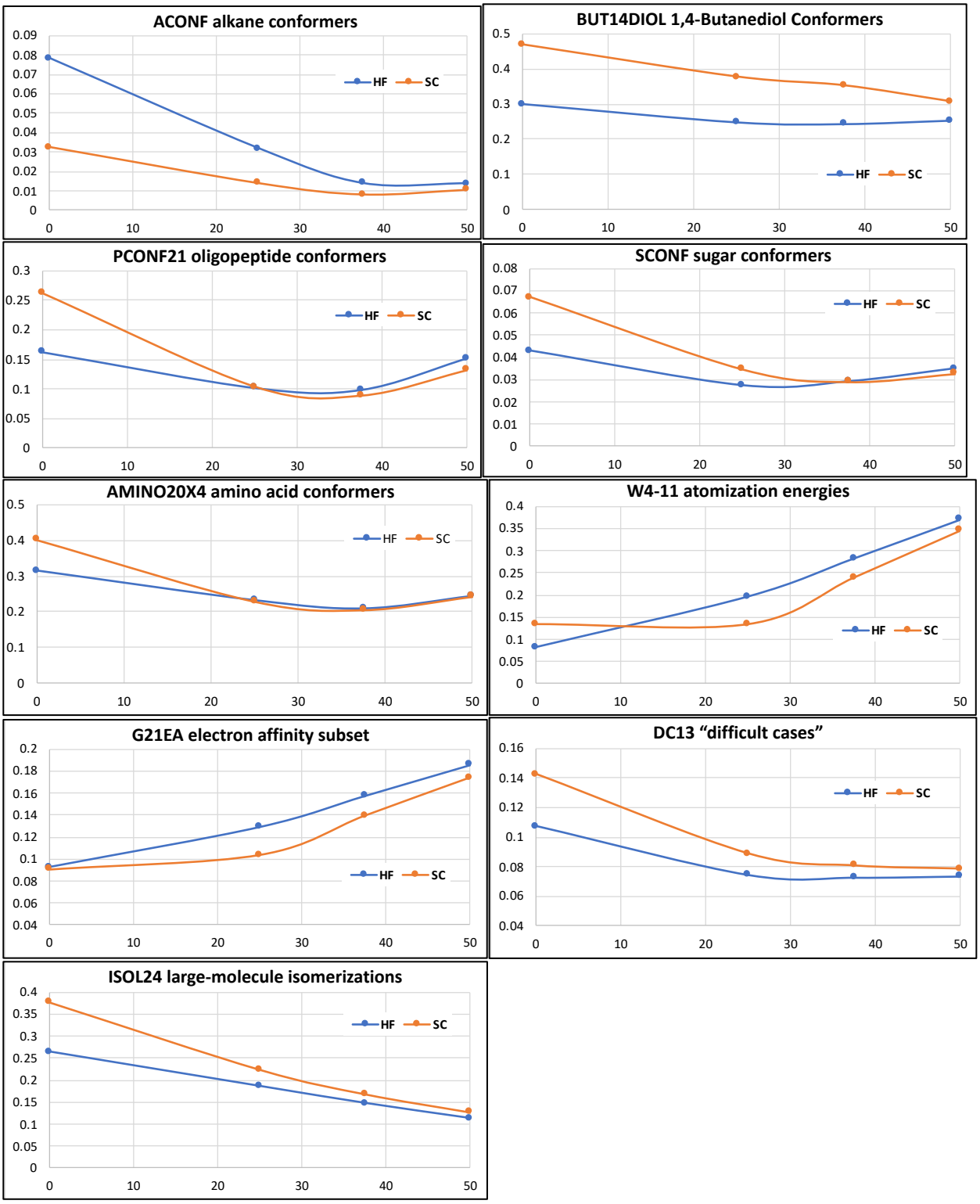
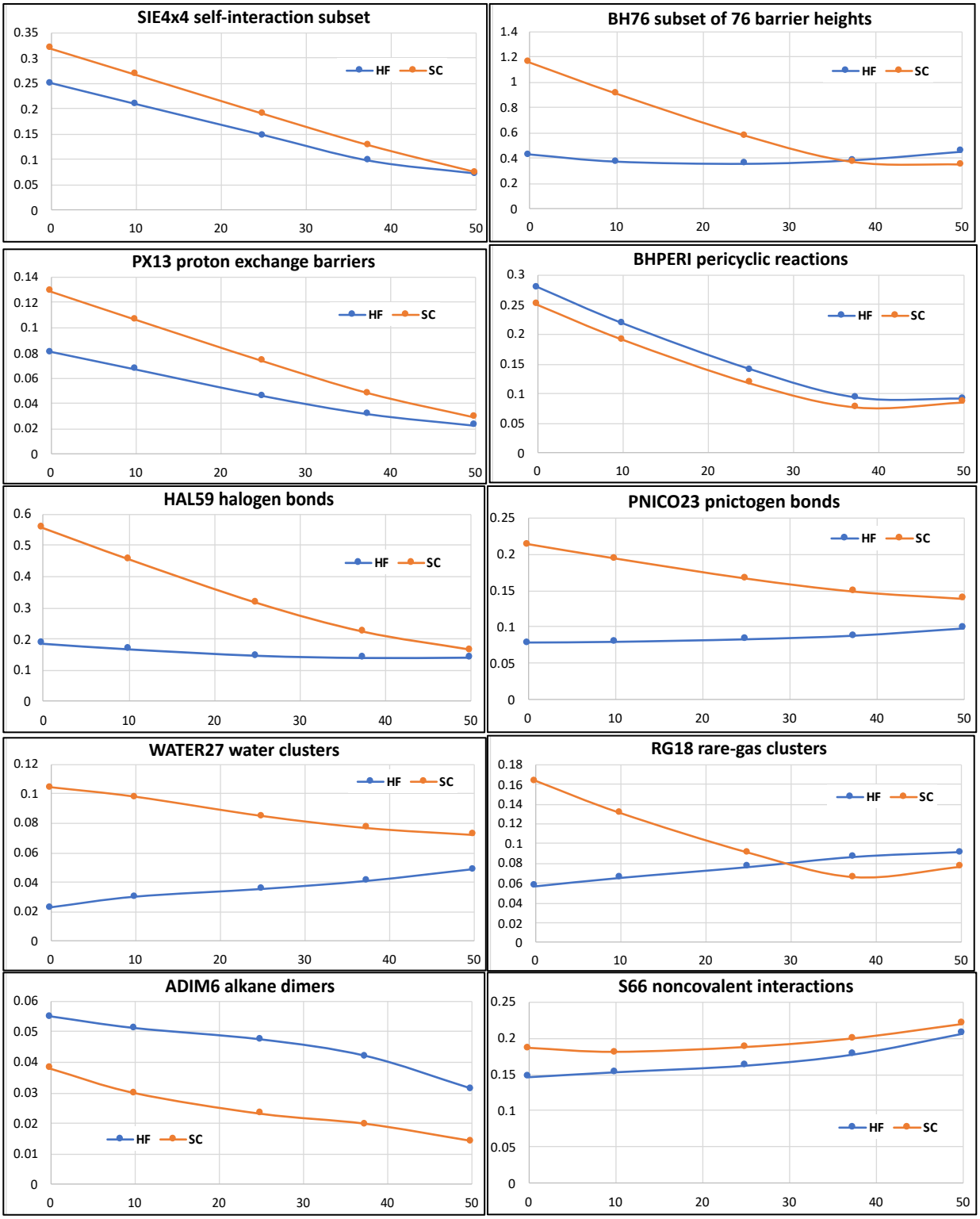


Figure S1: Dependence on the percentage of HF exchange, for self-consistent B*n*LYP-D4 and HF-B*n*LYP-D4 of the WTMAD2 (kcal/mol) contributions for the individual subsets SIE4x4, BH76, PX13, BHPERI, HAL59, PNICO23, W A TER27, RG18, ADIM6, S66, alkane conformers(ACONF), 1,4-butanediol conformers(BUT14DIOL), oligopeptide conformers

(PCONF21), sugar conformers(SCONF), amino acid conformers(AMINO20X4), G21EA, W4-11, DC13 and large molecule isomerization(ISOL24) subsets.



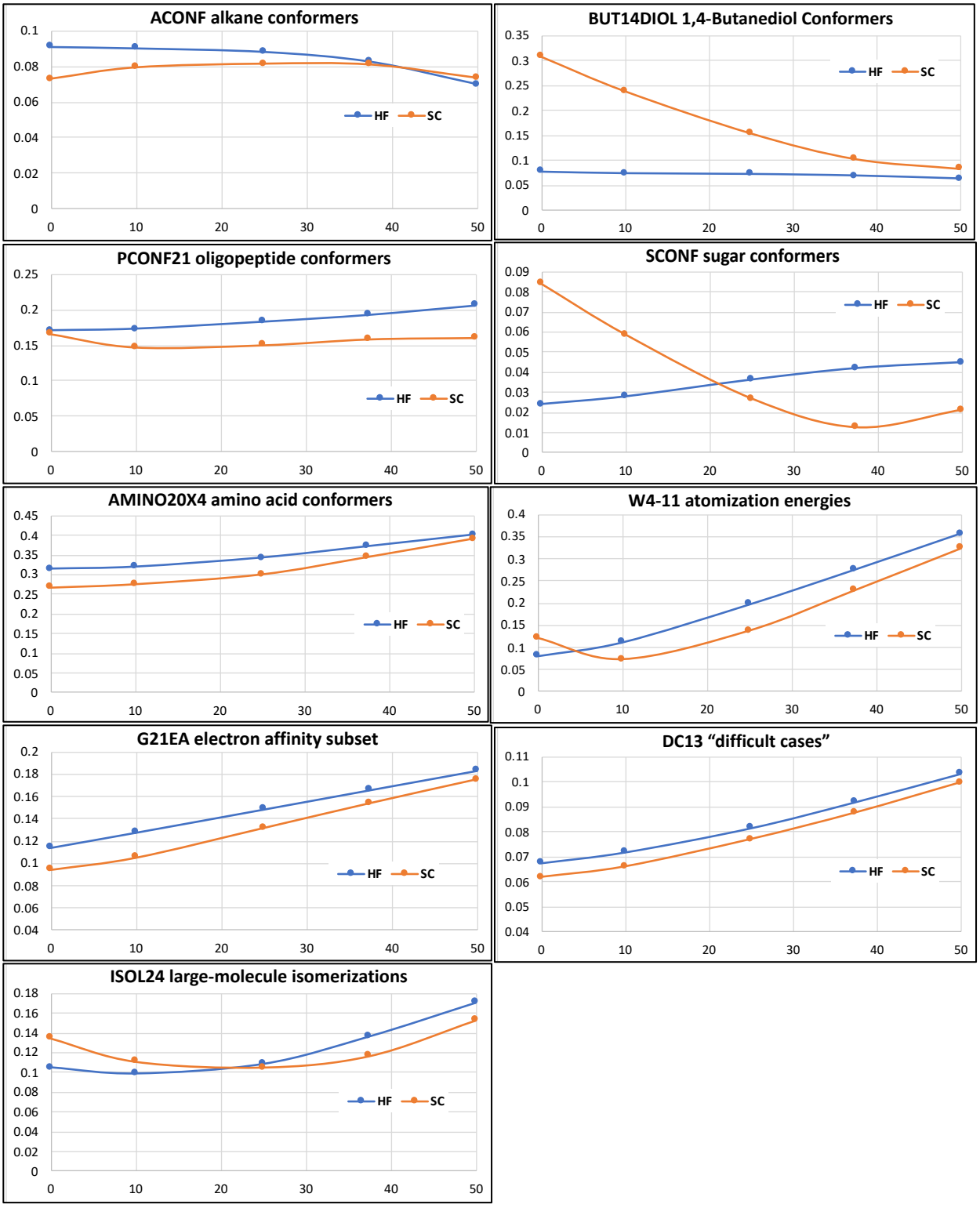


Figure S2: Dependence on the percentage of HF exchange, for self-consistent SCAN*n*-D4 and HF-SCAN*n*-D4 of the WTMAD2 (kcal/mol) contributions for the individual subsets SIE4x4, BH76, PX13, BHPERI, HAL59, PNICO23, W A TER27, RG18, ADIM6, S66, alkane conformers(ACONF), 1,4-butanediol conformers(BUT14DIOL), oligopeptide conformers (PCONF21), sugar conformers(SCONF), amino acid conformers(AMINO20X4), G21EA, W4-11, DC13 and large molecule isomerization(ISOL24) subsets.

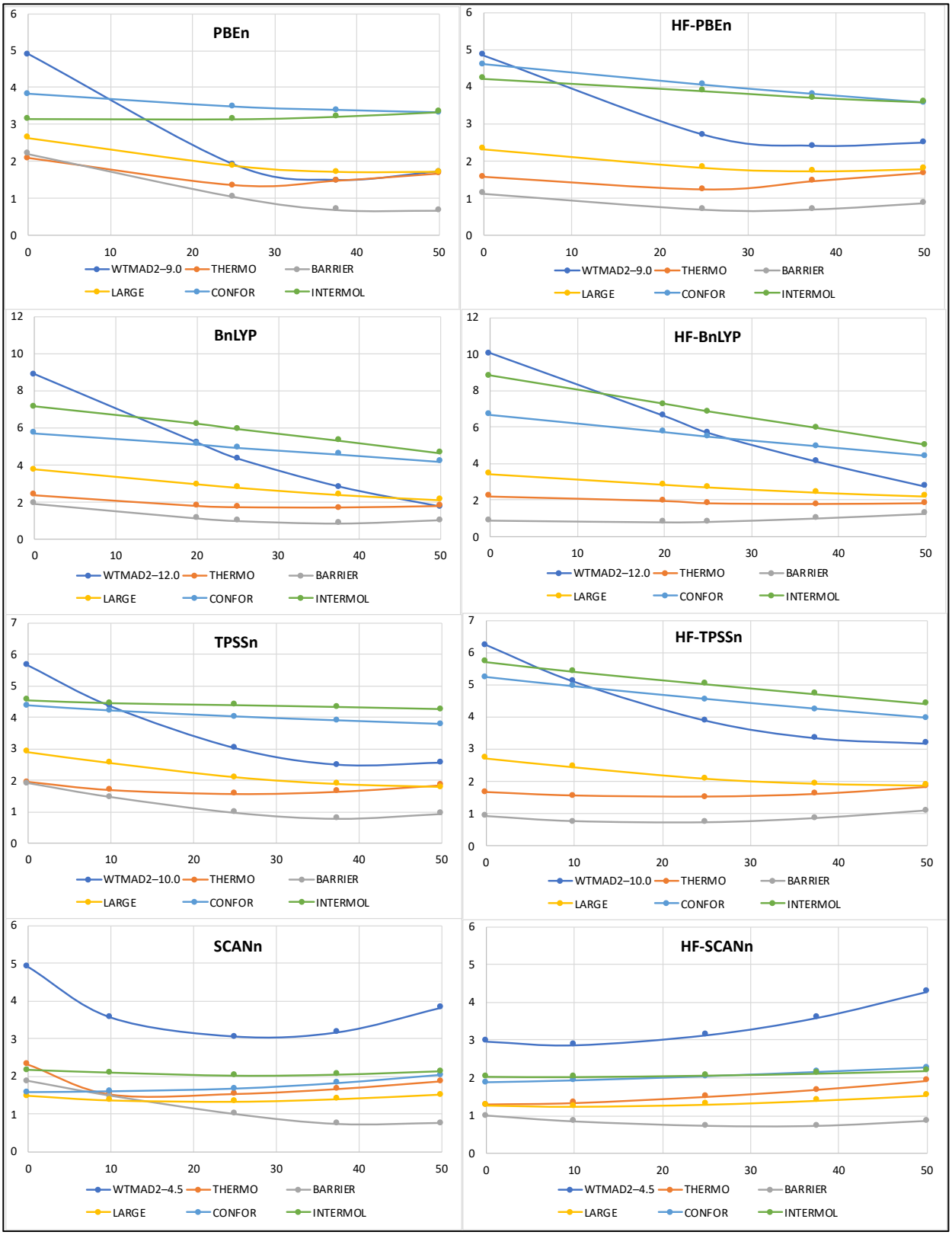


Figure S3: Dependence of WTMAD2 (kcal/mol) and of the five top-level subsets on the percentage of HF exchange(x-axis) for dispersion free PBE, BLYP, TPSS and SCAN series.

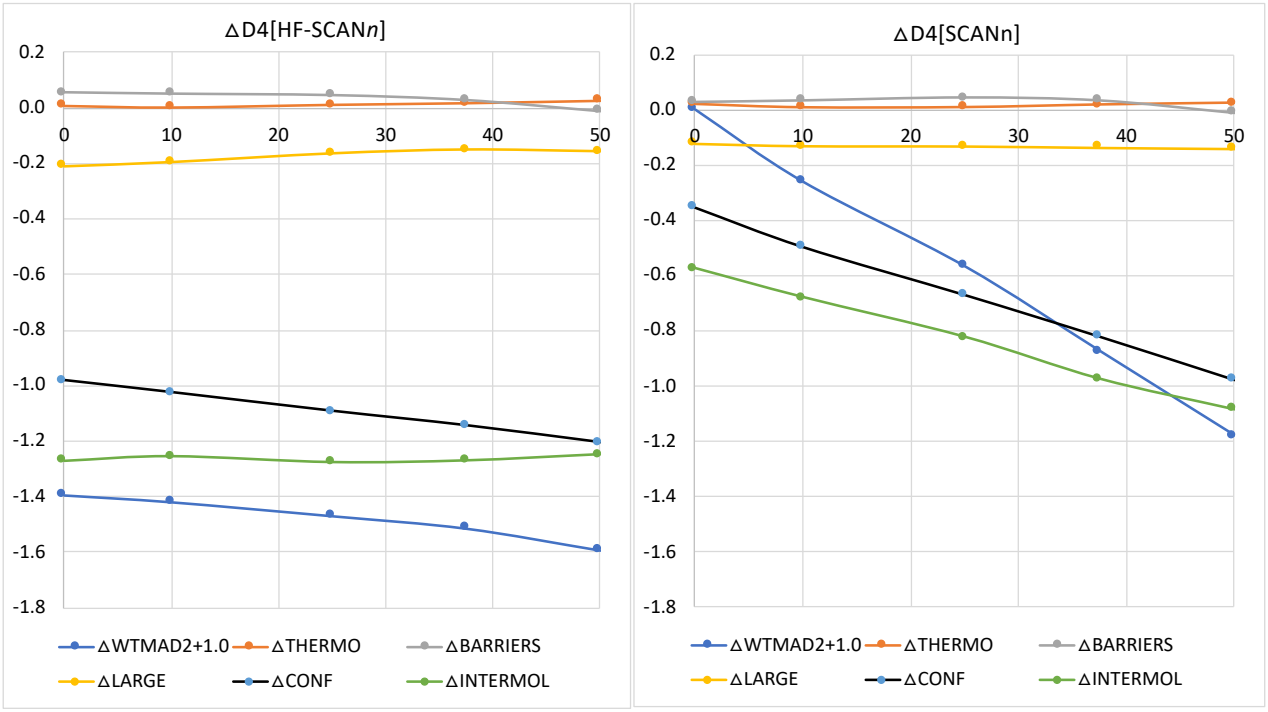


Figure S4: The effect of considering D4 dispersion correction on top of SCAN*n* and HF-SCAN*n* for different percentage of HF exchange.

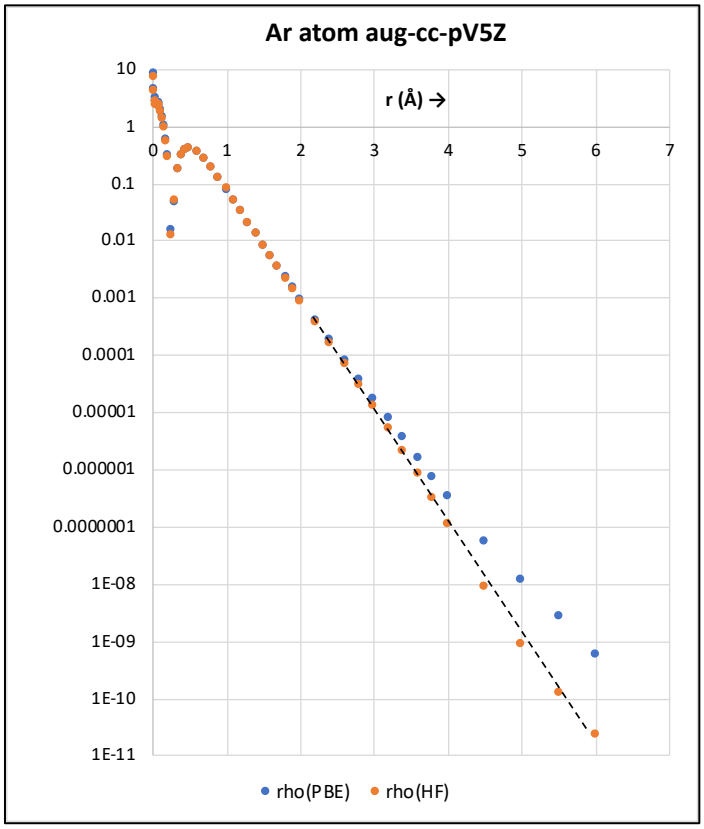


Figure S5: Decay trend of pure HF density and self-consistent PBE density for Ar atom

HF-DFT

A. Gaussian Sample Inputs:

1. PBE-D3BJ

```
%chk=file.chk
#p hf nosymm Def2QZVPP guess=save

title

0 1
 C    0.000000000000    0.000000000000     0.000000000000
 O    0.000000000000    0.000000000000     1.131400000000

--Link1—

%chk=file.chk
#p empiricaldispersion=gd3bj pbepbe Def2QZVPP scf(maxcycle=-1)
geom=allcheck guess=read
```

2. PBE38-D3BJ

```
%chk=file.chk
%mem=16gb
#p hf nosymm Def2QZVPP guess=save

title

0 1
 C    0.000000000000     0.000000000000     0.000000000000
 O    0.000000000000     0.000000000000     1.131400000000

--Link1—

%chk=file.chk
#p pbe1pbe iop(3/78=1000010000,3/76=0625003750,3/77=1000010000)
# empiricaldispersion=gd3bj
iop(3/174=1000000,3/175=1462300,3/177=0399500,3/178=5140500)
# iop(8/117=-100)
# scf(maxcycle=-1) chkbas geom=allcheck guess=read
```

B. ORCA Sample input:

1. TPSS-D3BJ

```
! UHF def2-QZVPP def2/J TightSCF NoPop XYZFILE

* xyz 0 1
 C    0.000000000000      0.000000000000     0.000000000000
 O    0.000000000000      0.000000000000     1.131400000000
*

$new_job
! UKS TPSS D3BJ def2-QZVPP def2/J grid5 moread NoPop

%scf
 maxiter 1
 tole 10000
 tolg 10000
end

* xyzfile 0 1
```

2. TPSS38

```
! UHF def2-QZVPP def2/JK TightSCF NoPop XYZFILE

* xyz 0 1
 C    0.000000000000    0.000000000000     0.000000000000
 O    0.000000000000    0.000000000000     1.131400000000
*

$new_job

! UKS TPSS0 def2-QZVPP def2/JK grid5 moread NoPop

%method
   Exchange X_TPSS
   Correlation C_TPSS
   ScalHFX 0.375
   ScalDFX 0.625
   ScalGGAC 1.0000
   ScalLDAC 1.0000
end
```

```
%scf
 maxiter 1
 tole 10000
 tolg 10000
end

* xyzfile 0 1
```

References:

(1) Gruzman, D.; Karton, A.; Martin, J. M. L. Performance of Ab Initio and Density Functional Methods for Conformational Equilibria of C n H 2 n +2 Alkane Isomers (n = 4−8) †. *J. Phys. Chem. A* **2009**, *113*, 11974–11983.

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