

(continued from previous page)

```

LDAOpt C_PWLDA
ScalHFX      0.00 # fraction of static Hartree-Fock exchange
ScalDFX      0.00 # fraction of static GGA exchange
ScalGGAC     1.00 # fraction of GGA correlation
ScalLDAC     1.00 # fraction of LDA correlation, must be equal to ScalGGAC
RangeSepEXX  true # activates range-separated exchange
RangeSepMu   0.47 # range-separation parameter, should be >0
RangeSepScal 1.00 # fraction of variable HFX, should sum to 1 with ScalHFX_
↪and ScalDFX
end

```

Warning

The amount of fixed DFT Exchange (ACM_B or ScalDFX) can only be changed for CAM-B3LYP and LC-BLYP. Accordingly, ACM-B is ignored by the ω B97 approaches as no corresponding μ -independent exchange functional has been defined. While it is technically possible to choose an exchange functional that has no μ -dependence, this makes no sense conceptually.

Table 3.7: %method block input keywords to modify range-separated hybrid functionals.

Keyword	Options	Description
RangeSepEXX	true	Activates range-separated exchange
RangeSepMu	<real>	Controls the range-separation parameter, should be >0
RangeSepScal	<real>	Controls the fraction of variable Hartree-Fock exchange

3.3.5 Double-Hybrid DFT

In addition to mixing the HF-exchange into a given density functional, Grimme has proposed to mix in a fraction of the *MP2 correlation energy* as calculated with hybrid DFT orbitals [249]. Such functionals may be referred to as “double-“hybrid functionals. The original expression by Grimme is:

$$E_{XC} = aE_X^{\text{HF}} + (1 - a) E_X^{\text{DFT}} + (1 - c) E_C^{\text{DFT}} + cE_C^{\text{MP2}} \quad (3.8)$$

The first proposed double-hybrid functional by Grimme was B2PLYP.[249] This double-hybrid functional utilizes the B88 exchange functional and the LYP correlation functionals. It introduces 53% of Hartree-Fock exchange ($a = 0.53$) and replaces 27% of the DFT correlation energy by MP2 correlation energy ($c = 0.27$). Since then many other DH-DFT approaches that deviate from the original theme were developed. For example Grimme proposed DH functionals like PWPB95[250] that use spin-component-scaled MP2. Further, functionals whose composition was empirically fitted against databases without any physical constraints or restrictions as previously proposed in (3.8) like Martin’s DSD (dispersion corrected, spin-component scaled double-hybrid) functionals[251, 252, 253] were developed and refined with revDSD-PBEP86-D4[254] being one of the most well known representatives. Functionals of the XYGn family[255] or Head-Gordon’s ω B97M(2)[256] employ differently constructed densities for the DFT and the perturbation-theory parts with the latter also basing on a *range-separated hybrid functional*. In principle, other correlated methods like dRPA or higher order MP theory may be used within the double hybrid scheme. However, the most common approach employs classical *MP2* or its spin-component-scaled variants. The *DLPNO approximation to MP2* is also available within ORCA and can be used to massively speed up the energy and gradient calculations for large systems. The accuracy and efficiency of DLPNO-DHs was extensively studied by Bursch, Neese and co-workers[257]. Common to almost all double-hybrid functionals is a comparably large amount of Hartree-Fock exchange of 50% and more. Most classical double-hybrid functionals following the scheme by Grimme can be utilized for single point calculations, analytic gradients (and thus also geometry optimizations[258], relaxed scans, and transition state searches), dipole moments and other first order properties, magnetic second order properties (chemical shifts and g-tensors without the frozen core approximation in the MP2 part), as well as for numerical polarizabilities and frequencies.

Some double-hybrid functionals were further optimized for excited state applications and will make use of a *Doubles Corrections* to correct the singles-only excited states within the *time-dependent DFT (TD-DFT)* framework. Some of them, like SCS-PBE-QIDH only make use of spin-component-scaling for the CIS(D) component of the calculation. However, many of them have recently also been tested for ground-state properties.[259]

Note

ORCA employs the *RIJCOSX* and *RI-MP2* by default. If this is not wanted, RI can be deactivated generally by using the `!NORI` keyword or if only the RI approximation of the MP2 part should be deactivated via the `%mp2` block:

```
%mp2
  RI false
end
```

Indeed, there is hardly ever any reason to use conventional MP2.

Note

Note that per default no MP2 response density is calculated as its construction adds significant overhead. In this case, only the double-hybrid energy is correct. The computation of the MP2 response density that is consistent with first-order properties from analytic first-derivatives can be requested via the `%mp2 density relaxed end` statement in the `%mp2` block. The considerably less costly unrelaxed (expectation value-like) density may instead requested by `%mp2 density unrelaxed end`. However, this is not recommended since the changes to the relaxed density are considerable in our experience and the unrelaxed density has a much weaker theoretical status than its relaxed counterpart.

Global Double-Hybrid Functionals

Global double-hybrid functionals are based on the respective *global hybrid functionals* and employ static admixtures of *Hartree-Fock* exchange and *the MP2 correlation energy*. A list of currently implemented global double-hybrid functionals is given in Table 3.8. The revDSD-PBEP86-D4[254] by Martin and co-workers has proven to be accurate for most thermochemistry applications.

Warning

For some functionals of the DSD/DOD family, different parameters for the same functional name were provided by the authors. The employed parameterization is indicated by the `(year-of-publication)` suffix of the functional and the respective keywords. Also not that for some of them, the basic parameters change in presence of different *dispersion corrections*. Please carefully check, if the employed parameters agree with your expectations!

Hint

For most natively implemented double-hybrids you can simply add the `DLPNO-` prefix to the respective functional simple input keyword, e.g. `DLPNO-B2PLYP`. For all others, the DLPNO treatment can be activated via the `%mp2` block using the `DLPNO true` keyword.

Table 3.8: List of available global double-hybrid functionals. PS is the opposite-spin, PT the same-spin scaling parameter. Excited-states optimized functionals only employ spin-component-scaling for the CIS(D) doubles correction within the the TD-DFT framework. Same-spin indirect term (CTss), opposite-spin indirect term (CTos), same-spin direct term (CUss), and opposite-spin direct term (CUos) parameters are given in the footnotes.

Functional	Keywords	%HFX	%DFX	%GGAC	%MP2C	PS	PT
DSD-BLYP [251]	DSD-BLYP D3BJ	69	31	54	100	0.46	0.37
DSD-BLYP- NoDisp(2013) [253]	DSD-BLYP, 2013	75	25	53	100	0.46	0.60
DSD-BLYP- D3(BJ)(2013) [253]	DSD-BLYP, 2013 D3BJ	71	29	54	100	0.47	0.40
DSD-PBEP86 [252]	DSD-PBEP86 D3BJ	70	30	43	100	0.53	0.25
DSD-PBEP86- NoDisp(2013) [253]	DSD-PBEP86, 2013	72	28	44	100	0.51	0.36
DSD-PBEP86- D3(BJ)(2013) [253]	DSD-PBEP86, 2013 D3BJ	69	31	44	100	0.52	0.22
DSD-PBEB95- NoDisp [253]	DSD-PBEB95	70	30	52	100	0.48	0.22
DSD-PBEB95- D3(BJ) [253]	DSD-PBEB95 D3BJ	66	34	55	100	0.46	0.09
B2PLYP [249]	B2PLYP	53	47	73	27	–	–
mPW2PLYP [260]	mPW2PLYP	55	45	75	25	–	–
B2GP- PLYP [261]	B2GP-PLYP	65	35	64	36	–	–
B2K- PLYP [262]	B2K-PLYP	72	28	58	42	–	–
B2T- PLYP [262]	B2T-PLYP	60	40	69	31	–	–
B2NC- PLYP [263]	B2NC-PLYP	81	19	45	55	–	–
PWPB95 [250]	PWPB95	50	50	73.1	26.9	1.0	0.0

continues on next page

Table 3.8 – continued from previous page

Functional	Keywords	%HFX	%DFX	%GGAC	%MP2C	PS	PT
PBE-QIDH [264]	PBE-QIDH	69	31	67	33	–	–
PBE0-DH [265]	PBE0-DH	50	50	87.5	12.5	–	–
revDSD-PBEP86(2021) [254]	REVDSD-PBEP86(2021)	69	31	42.24	100	0.5935	0.0566
revDSD-PBEP86-D4(2021) [254]	REVDSD-PBEP86-D4(2021)	69	31	42.24	100	0.5935	0.0566
revDOD-PBEP86(2021) [254]	REVDOD-PBEP86(2021)	69	31	43.01	100	0.6131	0.0
revDOD-PBEP86-D4(2021) [254]	REVDOD-PBEP86-D4(2021)	69	31	43.01	100	0.6131	0.0
SOS1-r ² SCAN-CIDH [248]	R2SCAN-CIDH	55	45	83.33	16.67	1.333	0.0
SOS1-r ² SCAN-QIDH [248]	R2SCAN-QIDH	69.34	30.76	66.67	33.33	1.333	0.0
SOS1-r ² SCAN0-2 [248]	R2SCAN0-2	79.37	20.63	50	50	1.333	0.0
SOS1-r ² SCAN0-DH [248]	R2SCAN0-DH	50	50	87.50	12.50	1.333	0.0
Pr ² SCAN50 [248]	PR2SCAN50	50	50	75	25	1.333	0.0
Pr ² SCAN69 [248]	PR2SCAN69	69.34	30.76	55.56	44.44	1.333	0.0
κPr ² SCAN50 [248]	KPR2SCAN50	50	50	70	30	1.333	0.0
excited state opt.							
SCS/SOS-B2PLYP21 [266]	SCS/SOS-B2PLYP21	53	47	73	27	1	Page 227, 1
SCS-PBE-QIDH [266]	SCS-PBE-QIDH	69	31	67	33	2	Page 227, 2
SOS-PBE-QIDH [266]	SOS-PBE-QIDH	69	31	67	33	3	Page 227, 3
SCS-B2GP-PLYP21 [266]	SCS-B2GP-PLYP21	65	35	64	36	4	Page 227, 4

continues on next page

Table 3.8 – continued from previous page

Functional	Keywords	%HFX	%DFX	%GGAC	%MP2C	PS	PT
SOS-B2GP-PLYP21 [266]	SOS-B2GP-	65	35	64	36	5	5

Range-Separated Double-Hybrid Functionals

Range-separated double-hybrids employ variable amounts of Hartree-Fock exchange much like *range-separated hybrid functionals* and static amounts of *MP2 correlation*. A list of available range-separated double-hybrid functionals is given in Table 3.9.

Hint

For most natively implemented double-hybrids you can simply add the DLPNO- prefix to the respective functional simple input keyword, e.g. DLPNO-WP2SCAN50. For all others, the DLPNO treatment can be activated via the %mp2 block using the DLPNO true keyword.

Table 3.9: List of available range-separated double-hybrid functionals. PS is the opposite-spin, PT the same-spin scaling parameter. μ is the range-separation parameter. Excited-states optimized (ES-Opt.) functionals only employ spin-component-scaling for the CIS(D) doubles correction within the TD-DFT framework. Same-spin indirect term (CTss), opposite-spin indirect term (CTos), same-spin direct term (CUss), and opposite-spin direct term (CUos) parameters are given in the footnotes.

¹ SCS/SOS-B2PLYP21: CTss: 0.000; CTos: 0.334; CUss: 0.000; CUos: 0.283.

² SCS-PBE-QIDH: CTss: 0.070; CTos: 0.515; CUss: 0.096; CUos: 0.524.

³ SOS-PBE-QIDH: CTss: 0.000; CTos: 0.547; CUss: 0.000; CUos: 0.573.

⁴ SCS-B2GP-PLYP21: CTss: 0.018; CTos: 0.475; CUss: 0.000; CUos: 0.468.

⁵ SOS-B2GP-PLYP21: CTss: 0.000; CTos: 0.489; CUss: 0.000; CUos: 0.484.

Functional	Keywords	%HFX	μ bohr ⁻¹	%GGAC	%MP2C	PS	PT
ω B97M(2) ⁶ [256]	WB97M(2)	62.194 – 100	0.30	100	34.096	–	–
ω B97X-2(TQZ) [267]	WB97X-2	63.6158 – 95.1661	– 0.30	100	100	0.44710	0.529319
ω Pr2SCAN50 [248]	WPR2SCAN50	50 – 100	0.214013	65	35	1.333	0.000
RSX-QIDH [268]	RSX-QIDH	69 – 100	0.27	67	33	–	–
RSX-0DH [269]	RSX-0DH	50 – 100	0.33	87.5	12.5	–	–
ω B2PLYP [270]	WB2PLYP	53 – 100	0.30	73	27	–	–
ω B2GP-PLYP [270]	WB2GP-PLYP	65 – 100	0.27	64	36	–	–
ω B88PP86 [270]	WB88PP86	65 – 100	0.20	58	42	–	–
ω PBEP86 [270]	WPBEP86	70 – 100	0.18	68	48	–	–
excited state opt.							
SCS/SOS- ω B2PLYP [266]	SCS/ SOS-WB2PLYP	53 – 100	0.30	73	27	7	7
SCS- ω B2GP-PLYP [266]	SCS-WB2GP-PLYP	65 – 100	0.27	64	36	8	8
SOS- ω B2GP-PLYP [266]	SOS-WB2GP-PLYP	65 – 100	0.27	64	36	9	9
SCS-RSX-QIDH [266]	SCS-RSX-QIDH	69 – 100	0.27	67	33	10	10
SOS-RSX-QIDH [266]	SOS-RSX-QIDH	69 – 100	0.27	67	33	11	11
SCS- ω B88PP86 [266]	SCS-WB88PP86	65 – 100	0.20	58	42	12	12
SOS- ω B88PP86 [266]	SOS-WB88PP86	65 – 100	0.20	58	42	13	13
SCS- ω PBEP86 [266]	SCS-WPBEP86	70 – 100	0.18	68	48	14	14
SOS- ω PBEP86 [266]	SOS-WPBEP86	70 – 100	0.18	68	48	15	15

ω B97M(2)

Some double-hybrid functionals, such as ω B97M(2)[256] must be applied to orbitals converged with a different functional. This can be accomplished with a two-step calculation using `MORead` and `MaxIter=1`. Note that because the orbitals are not obtained self-consistently, only single point energies can be computed in this way, i.e. no density, gradient, or properties! The usage of such functionals may be automatized using the *Compound script language*. An exemplary compound script for a ω B97M(2) single-point calculation is given below:

```
*xyz 0 1
  H 0.0 0.0 0.0
  F 0.0 0.0 0.9
*
# -----
```

(continues on next page)

⁶ Must be used with ω B97M-V orbitals (cf. Section 3.3.5).

⁷ SCS/SOS- ω B2PLYP: CTss: 0.000; CTos: 0.433; CUss: 0.000; CUos: 0.460.

⁸ SCS- ω B2GP-PLYP: CTss: 0.000; CTos: 0.571; CUss: 0.135; CUos: 0.558.

⁹ SOS- ω B2GP-PLYP: CTss: 0.000; CTos: 0.570; CUss: 0.000; CUos: 0.610.

¹⁰ SCS-RSX-QIDH: CTss: 0.174; CTos: 0.541; CUss: 0.586; CUos: 0.424.

¹¹ SOS-RSX-QIDH: CTss: 0.000; CTos: 0.632; CUss: 0.000; CUos: 0.714.

¹² SCS- ω B88PP86: CTss: 0.000; CTos: 0.557; CUss: 0.092; CUos: 0.545.

¹³ SOS- ω B88PP86: CTss: 0.000; CTos: 0.559; CUss: 0.000; CUos: 0.599.

¹⁴ SCS- ω PBEP86: CTss: 0.000; CTos: 0.610; CUss: 0.297; CUos: 0.540.

¹⁵ SOS- ω PBEP86: CTss: 0.000; CTos: 0.613; CUss: 0.000; CUos: 0.669.

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```

↪---
# Energy calculation with the wB97M(2) double-hybrid functional, as defined in
# N. Mardirossian, M. Head-Gordon, J. Chem. Phys. 2018, 148, 241736.
# The final energy is calculated non-variationally using wB97M-V orbitals.
# Note that FrozenCore is on default - one can turn it off using kw2 =
↪"NoFrozenCore".
# Author: Georgi L. Stoychev
# -----
↪---

# Optional variables:
Variable NLOpt = "SCNL";          # Consistent with Q-Chem. "NL" likely very similar.
↪ Only matters for Step 1.
Variable Basis = "def2-TZVP";    # Should be TZ or higher for reliable results
Variable AuxC = "def2-TZVP/C";   # RI-MP2 is used by default. Must be compatible_
↪with the Basis
Variable AuxJ = "def2/J";        # RIJCOSX is used by default
Variable RIMP2 = True;           # Set to false to turn off RI-MP2
Variable Grid = "defGrid2";      # Should be OK.
Variable kw1 = "";              # Additional simple input keywords for step 1
Variable kw2 = "";              # Additional simple input keywords for step 2

# Output variables
Variable EwB97MV, EwB97M2;      # Will hold the final energies

# Step 1: wB97M-V calculation to obtain the orbitals
New_Step
! wB97M-V &{NLOpt} &{Grid} &{kw1}
%basis
  Basis "&{Basis}"
  AuxJ "&{AuxJ}"
end
Step_End

# Step 2: single iteration with the wB97M(2) functional + MP2 correlation to get_
↪the final energy
ReadMOs(1);
New_Step
! wB97M(2) &{NLOpt} &{Grid} &{kw2} NoIter CalcGuessEnergy
%basis
  Basis "&{Basis}"
  AuxC "&{AuxC}"
  AuxJ "&{AuxJ}"
end
%scf
  IgnoreConv 1
end
%mp2 RI &{RIMP2} end
Step_End

Read EwB97MV = DFT_Total_En[1];
Read EwB97M2 = MP2_Total_Energy[2];

Print("");
Print(
↪"=====\\
↪n");
Print(" wB97M-V Energy: %20.10lf\\n",EwB97MV);
Print(" wB97M(2) Energy: %20.10lf\\n",EwB97M2);

End

```

Customization of Double-Hybrids

As double-hybrid functionals make use of customizable components of *global hybrids* or *range-separated hybrids* they can be constructed and customized in similar fashion. The MP2 correlation treatment for double-hybrids can be controlled via the `DoMP2 true` and `ScalMP2C` keywords within the `%method` block. Moreover, the MP2 treatment can be further customized via the `%mp2` block. For example, the spin-composite-scaled, range-separated double-hybrid functional ω Pr²SCAN50 can be constructed as follows:

```
! RIJCOSX def2-TZVP/C NOTRAH
# wPr2SCAN50
%method
  Method      DFT
  DoMP2        true      # activates MP2 correlation part
  Exchange     X_WR2SCAN
  Correlation   C_R2SCAN
  LDAOpt       C_PWLDA
  ScalHFX      0.50      # fraction of static Hartree-Fock exchange
  ScalDFX      0.00      # fraction of static GGA exchange
  ScalGGAC     0.65      # fraction of GGA correlation
  ScalLDAC     0.65      # fraction of LDA correlation, must be equal to ScalGGAC
  ScalMP2C     0.35      # fraction of MP2 correlation
  RangeSepEXX  true      # activates range-separated exchange
  RangeSepMu   0.214013  # range-separation parameter, should be >0
  RangeSepScal 0.50      # fraction of variable HFX, should sum to 1 with
  ↪ScalHFX and ScalDFX
end
%mp2
  DoSCS        true      # activates spin-component-scaling
  RI            true      # activate RI-MP2
  PS            1.333     # opposite-spin-scaling parameter
  PT            0.000     # same-spin-scaling parameter
end
```

Many other MP2 related options like the DLPNO treatment and regularization can be found in the [MP2](#) section of the manual.

Table 3.10: Most important `%method` block input keywords to customize double-hybrid functionals.

Keyword	Options	Description
DoMP2	true	Activates MP2 correlation part
ScalMP2C	<real>	Controls the fraction of GGA exchange

Table 3.11: Most important `%mp2` block input keywords to customize double-hybrid functionals. For more details see the MP2 section.

Keyword	Options	Description
DoSCS	true	Activates spin-component-scaling of MP2 part
PS	<real>	Controls the opposite-spin-scaling parameter
PT	<real>	Controls the same-spin-scaling parameter
RI	true	Activates RI-MP2
DLPNO	true	Activates DLPNO-MP2

3.3.6 LibXC Functional Library

It is possible to use the functionals provided by LibXC within the ORCA framework¹⁶. The LibXC version used by ORCA is printed at the beginning of the output. The LibXC reference should be cited when LibXC is used as part of your calculations. For reference, see [271].

The complete list of functionals available via the LibXC interface can always be inspected by typing at the command line

```
orca -libxcfunctionals
```

The list of functionals has the following form:

Functionals available via LibXC:

No.:	ID / Keyword	- Name
0:	18 / lda_c_1d_csc	- Casula, Sorella & Senatore
1:	26 / lda_c_1d_loos	- P-F Loos correlation LDA
2:	15 / lda_c_2d_amgb	- AMGB (for 2D systems)
3:	16 / lda_c_2d_prm	- PRM (for 2D systems)
4:	552 / lda_c_br78	- Brual & Rothstein 78
...		

The list is grouped by “level” of functional (LDA, GGA, meta-GGA, etc.) and then by part of the energy it models (correlation, exchange, exchange-correlation). Correlation functionals carry a ‘_c_’ in their names, exchange functionals an ‘_x_’, and combined exchange-correlation functionals an ‘_xc_’. Additional information for a specific functional can be requested using

```
orca -libxcinfo [functional name]
```

where the functional name is the keyword in the above list.

Specification of LibXC functionals in the ORCA input follows the standard format:

```
%method
  Method      DFT
  Functional  hyb_gga_xc_b3lyp
end
```

or in the case of separate exchange and correlation specifications:

```
%method
  Method      DFT
  Exchange    mgga_x_m06_l
  Correlation mgga_c_m06_l
end
```

CAM-type range-separated functionals are supported through the LibXC interface since ORCA 5.0. So are functionals that include non-local (VV10) correlation (see *Non-Local Dispersion Correction (VV10): DFT-NL*). The VV10 part is computed internally by ORCA. Other non-local functionals, such as BEEF-vdW, are not supported. Meta-GGA functionals that depend on the kinetic energy density τ are supported, but not those that depend on the Laplacian of the density $\nabla^2\rho$.

Double-hybrid functionals can be constructed with LibXC components as described in the previous customization sections, but only with separate exchange and correlation components. So `exchange=gga_x_pbe` and `correlation=gga_c_pbe` can be used, but `functional=hyb_gga_xc_pbeh` **cannot** be used in a double-hybrid formulation. Beware that the exchange and correlation contributions calculated by LibXC are simply scaled by `ScalDFX` and `ScalGGAC`, respectively, and no care is taken to separately scale LDA components or alter other internal parameters!

¹⁶ <https://libxc.gitlab.io>

Screening Thresholds

When the density is smaller than a certain threshold, LibXC skips the evaluation of the functional and instead sets all the output quantities to zero in order to avoid under- and/or overflows. The default thresholds for different functionals are set by the LibXC developers, but may sometimes be too low. We have not performed extensive testing, but allow the user to set the threshold. Similarly, there are thresholds for minimum values of ζ and τ in order to avoid division by zero. The default values are functional-independent and can be changed using the following keywords.

```
%method
  LibXCDensityThreshold 1e-12    # seems to be reasonable
  LibXCZetaThreshold    2e-16    # default value in LibXC
  LibXCTauThreshold     1e-20    # default value in LibXC
end
```

Modifying LibXC Functional Parameters

Starting with ORCA 5.1 it is possible to modify the “external parameters” of a functional that the LibXC interface provides. The available parameters and their default values can be seen in the output or with the `orca -libxcinfo` command above. Please exercise caution when using this interface and if using a published functional reparametrization, make sure you can reproduce results from the original publication. The syntax requires one of the `ExtParamX`, `ExtParamC`, or `ExtParamXC` keywords (depending on which functional is modified), followed by the parameter name in quotation marks, and finally the new value. For example, here is an input for the PWPB95 double-hybrid functional, where the simple input keyword is used to set most parameters (such as the MP2 scaling factors) and only the exchange and correlation parameters of the mPW91 and B95 LibXC functionals, respectively, are modified.

```
! Opt PWPB95 def2-SVP def2-SVP/C

%method
  Exchange      gga_x_mpw91
  Correlation    mpga_c_bc95
  ExtParamX     "_bt"      0.00444
  ExtParamX     "_alpha"   19.823391
  ExtParamX     "_expo"    3.7868
  ExtParamC     "_css"     0.03241
  ExtParamC     "_copp"    0.00250
end

*xyz 0 1
  H 0 0 0
  F 0 0 0.9
*
```

Note that the variable definitions in LibXC may be different from the ones used internally in ORCA or in the original publication, due to various constant factors, etc. When in doubt, please consult the LibXC documentation or source code repository — we simply provide access to the interface.

Simple Input of LibXC Functionals

Some LibXC functionals are accessible via the simple input keyword `!LibXC(Keyword)`, e.g. `!LibXC(TPSS)`. The keywords match those of the natively implemented in ORCA. Using this syntax, parameters for the *DFT-D dispersion corrections* are also set automatically (if implemented). Table 3.12 lists the available functionals and their LibXC names.

Table 3.12: LibXC functionals available via the simple input `!LibXC(Keyword)`

Keyword	LibXC components	Notes
GGAs		

continues on next page

Table 3.12 – continued from previous page

Keyword	LibXC components	Notes
B97-D	gga_xc_b97_d	Uses D2
B97-D3	gga_xc_b97_d	Uses D3(0)
B97-D4	gga_xc_b97_d	Uses D4
BLYP	gga_x_b88 + gga_c_lyp	
KT2	gga_xc_kt2	
KT3	gga_xc_kt3	
PBE	gga_x_pbe + gga_c_pbe	
REVPBE	gga_x_pbe + gga_c_pbe	$\kappa=1.245$
XLYP	gga_xc_xlyp	
meta-GGAs		
B97M-V	mgga_xc_b97m_v	Uses VV10
B97M-D3BJ	mgga_xc_b97m_v	Uses D3(BJ)
B97M-D4	mgga_xc_b97m_v	Uses D4
M06L	mgga_x_m06_l + mgga_c_m06_l	
MN15L	mgga_x_mn15_l + mgga_c_mn15_l	
MTASK-LDA	mgga_x_mtask + lda_c_pw_mod	
MTASK-SCAN	mgga_x_mtask + mgga_c_scan	
REVTM	mgga_x_revtm + mgga_c_revtm	
R2SCAN	mgga_x_r2scan + mgga_c_r2scan	
RSCAN	mgga_x_rscan + mgga_c_rscan	
SCAN	mgga_x_scan + mgga_c_scan	
TASK-CCALDA	mgga_x_task + mgga_c_ccalda	
TASK-CC	mgga_x_task + mgga_c_cc	
TASK-LDA	mgga_x_task + lda_c_pw_mod	
TASK-SCAN	mgga_x_task + mgga_c_scan	
TM	mgga_x_tm + mgga_c_tm	
TPSS	mgga_x_tpss + mgga_c_tpss	
hybrid GGAs		
B1PW	gga_x_b88,gga_c_pw91	Custom mixing
B1PBE	gga_x_b88 + gga_c_pbe	Custom mixing
B3PW91	hyb_gga_xc_b3pw91	Custom mixing
B3LYP	hyb_gga_xc_b3lyp5	
B3LYP/G	hyb_gga_xc_b3lyp	
B3LYPS	hyb_gga_xc_b3lyps	B3LYP*, 15% HFX
B97	hyb_gga_xc_b97	
CAM-B3LYP	hyb_gga_xc_cam_b3lyp	Custom mixing
CASE21	hyb_gga_xc_case21	
G1LYP	gga_x_g96 + gga_c_lyp	Custom mixing
HSE06	hyb_gga_xc_hse06	
HSE12	hyb_gga_xc_hse12	
HSE12S	hyb_gga_xc_hse12s	
HSESOL	hyb_gga_xc_hse_sol	
KMLYP	hyb_gga_xc_kmlyp	
LB07	hyb_gga_xc_lb07	
LC-BLYP	hyb_gga_xc_lc_blyp	Custom mixing
MPW1LYP	hyb_gga_xc_mpw1lyp	Custom mixing
MPW1PW	hyb_gga_xc_mpw1pw	Custom mixing
PBE0	hyb_gga_xc_pbeh	
PBE38	hyb_gga_xc_pbe38	
PBE50	hyb_gga_xc_pbe50	
PW91_0	gga_x_pw91 + gga_c_pw91	Custom mixing
PW1PW	gga_x_pw91 + gga_c_pw91	Custom mixing
REVPBE0	gga_x_pbe,gga_c_pbe	$\kappa=1.245$
REVPBE38	gga_x_pbe,gga_c_pbe	37.5% HFX, $\kappa=1.245$
WHPBE0	hyb_gga_xc_whpbe0	

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Table 3.12 – continued from previous page

Keyword	LibXC components	Notes
WB97	hyb_gga_xc_wb97	
WB97X	hyb_gga_xc_wb97x	
WB97X-D3	hyb_gga_xc_wb97x_d3	Uses D3(0)
WB97X-V	hyb_gga_xc_wb97x_v	Uses VV10
WB97X-D3BJ	hyb_gga_xc_wb97x_v	Uses D3(BJ)
WB97X-D4	hyb_gga_xc_wb97x_v	Uses D4
WB97X-D4REV	hyb_gga_xc_wb97x_v	Uses D4 with revised parameters
hybrid meta-GGAs		
GAS22	hyb_mgga_xc_gas22	
M05	hyb_mgga_x_m05 + mgga_c_m05	
M052X	hyb_mgga_x_m05_2x + mgga_c_m05_2x	
M06	hyb_mgga_x_m06 + mgga_c_m06	
M062X	hyb_mgga_x_m06_2x + mgga_c_m06_2x	
M06SX	hyb_mgga_x_m06_sx + mgga_c_m06_sx	
MN15	hyb_mgga_x_mn15 + mgga_c_mn15	
LC-TMLYP	hyb_mgga_xc_lc_tmlyp	
PW6B95	hyb_mgga_xc_pw6b95	
R2SCANH	hyb_mgga_xc_r2scanh	
R2SCAN0	hyb_mgga_xc_r2scan0	
R2SCAN38	hyb_mgga_xc_r2scanh	37.5% HFX
R2SCAN50	hyb_mgga_xc_r2scan50	
SCAN0	hyb_mgga_x_scan0 + mgga_c_scan	
TPSS0	hyb_mgga_xc_tpss0	
TPSSH	hyb_mgga_xc_tpssh	
WB97M-V	hyb_mgga_xc_wb97m_v	Uses VV10
WB97M-D3BJ	hyb_mgga_xc_wb97m_v	Uses D3(BJ)
WB97M-D4	hyb_mgga_xc_wb97m_v	Uses D4
WB97M-D4REV	hyb_mgga_xc_wb97m_v	Uses D4 with revised parameters
double-hybrids		
B2PLYP	gga_x_b88 + gga_c_lyp	Custom mixing
B2GP-PLYP	gga_x_b88 + gga_c_lyp	Custom mixing
B2T-PLYP	gga_x_b88 + gga_c_lyp	Custom mixing
B2K-PLYP	gga_x_b88 + gga_c_lyp	Custom mixing
B2NC-PLYP	gga_x_b88 + gga_c_lyp	Custom mixing
DSD-PBEB95-D3	gga_x_pbe + mgga_c_bc95	Custom mixing, uses D3(BJ)
DSD-PBEB95-D4	gga_x_pbe + mgga_c_bc95	Custom mixing, uses D4
MPW2-PLYP	gga_x_mpw91 + gga_c_lyp	Custom mixing
PWPB95	gga_x_mpw91 + mgga_c_bc95	Custom mixing and ExtParam's
PBE0-DH	gga_x_pbe + gga_c_pbe	Custom mixing
PBE0-2	gga_x_pbe + gga_c_pbe	Custom mixing
PBE-QIDH	gga_x_pbe + gga_c_pbe	Custom mixing
PR2SCAN50	mgga_x_r2scan + mgga_c_r2scan	Custom mixing
PR2SCAN69	mgga_x_r2scan + mgga_c_r2scan	Custom mixing
SOS1-R2SCAN0-DH	mgga_x_r2scan + mgga_c_r2scan	Custom mixing
SOS1-R2SCAN-CIDH	mgga_x_r2scan + mgga_c_r2scan	Custom mixing
SOS1-R2SCAN-QIDH	mgga_x_r2scan + mgga_c_r2scan	Custom mixing
SOS1-R2SCAN0-2	mgga_x_r2scan + mgga_c_r2scan	Custom mixing

3.4 Dispersion Corrections

A major weakness of conventional density functional theory (and Hartree-Fock) is the lacking description of long-range correlation effects including London dispersion. London dispersion represents the attractive component of the van-der-Waals interaction and even though it is a rather weak interaction, its correct description can be crucial for many cases. This is specifically the case for non-covalent interactions and extended molecules. However, there are several well-established dispersion-corrections available to largely correct for this shortcoming. Within ORCA various options are available that include Grimme's D3 [272, 273] and D4 [159, 274] corrections as well as the non-local variant of VV10 (NL, [275, 276]) are available.

i Some notes on dispersion corrections

- Dispersion corrections do not only affect non-covalent complexes, but also conformational energies and structures which are heavily influenced by intramolecular dispersion. Therefore, including the dispersion correction is almost always recommended or even required (except for a handful of cases where it cannot, should not or need not be used, see below).
- DFT calculations with small basis sets (such as double- ζ basis sets) often yield attractive potential energy surfaces even without the dispersion correction. However, this is due to basis set superposition error (BSSE), and the interaction energy brought about by the BSSE frequently does not match the true interaction energy due to dispersion (because they have completely different origins). Therefore, although a DFT double zeta calculation without the dispersion correction may appear to give qualitatively correct results, or occasionally even better results than a double zeta calculation with dispersion corrections (because in the latter case one typically overestimates the total attraction), it is still highly recommended to “get the right answer for the right reason” by reducing the BSSE and turning on the dispersion correction. The BSSE can be corrected by a variety of means, for example (1) by using a larger basis set; (2) by using the counterpoise correction (*Counterpoise Corrections*); or (3) by using the geometrical counterpoise correction (section *Geometrical Counterpoise Correction (gCP)*). Of these, (3) is available at almost no cost (including analytic gradient contributions), and is especially suitable for geometry optimization of large molecules. Otherwise (1) (or its combination with (2)) may be more appropriate due to its higher accuracy.
- Functionals that contain VV10-type non-local dispersion (in general, these are the functionals whose names end with “-V”) do not need (and cannot be used together with) dispersion corrections. The same holds for post-HF and multireference methods, like MP2, CCSD(T), CASSCF and NEVPT2. However, one can add a dispersion correction on top of HF.
- Certain functionals, especially the Minnesota family of functionals (e.g. M06-2X), describe medium-range dispersion but miss long-range dispersion. They give reasonable dispersion energies for small to medium systems but may slightly underestimate the dispersion energies for large systems. As the uncorrected functional already accounts for the bulk of the dispersion in this case, the dispersion correction is much less important than e.g. the case of B3LYP, and should in general be considered as beneficial but not mandatory.

3.4.1 Grimme's DFT-D3 and DFT-D4

DFT-D3 and DFT-D4 are atom-pairwise (atom-triplewise) dispersion corrections which can be added to the KS-DFT energies and gradient [272]. In ORCA, D3 is available for all elements up to Pu ($Z = 94$) and D4 up to Lr ($Z = 103$).

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (3.9)$$

E_{disp} is then the sum of the two- and three-body contributions to the dispersion energy, $E_{\text{disp}} = E^{(2)} + E^{(3)}$. Most important is the two-body term, which is given at long range by:

$$E_{\text{disp}} = - \sum_{A < B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n} \quad (3.10)$$

where C_n^{AB} denotes the averaged (isotropic) n^{th} -order dispersion coefficient for atom pair AB and r_{AB} is their inter-nuclear distance. s_n is a functional-dependent scaling factor (see below). In the general case, an adequate damping

function must be employed. The more recent D4 model basically uses a similar theory but further introduces an atomic partial charge dependence of the atomic reference polarizabilities.

Damping Functions

In order to avoid near-singularities for small r_{AB} , the dispersion contribution needs to be damped at short distances. One possible way is to use rational damping as proposed by Becke and Johnson [277, 278, 279]:

$$E^{(2)} = - \sum_{A < B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n + f(R_0^{AB})^n} \quad (3.11)$$

with [279]

$$R_0^{AB} = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}} \quad (3.12)$$

and

$$f(R_0^{AB}) = a_1 R_0^{AB} + a_2. \quad (3.13)$$

Damping the dispersion contribution to zero for short ranges (as in Ref. [272]) is also possible:

$$E^{(2)} = - \sum_{A < B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n} f_{d,n}(r_{AB}) \quad (3.14)$$

with

$$f_{d,n} = \frac{1}{1 + 6 \left(\frac{r_{AB}}{s_{r,n} R_0^{AB}} \right)^{-\alpha_n}} \quad (3.15)$$

Note that the R_0^{AB} used with this damping are from Ref. [272]. For more information on the supported damping functions, see Ref [273].

Three-body term

It is possible to calculate the three-body dispersion contributions according to

$$E^{(3)} = - \sum_{A < B < C} \frac{C_9^{ABC} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3} f_{d,(3)}(\bar{r}_{ABC}) \quad (3.16)$$

where θ_a , θ_b and θ_c are the internal angles of the triangle formed by r_{AB} , r_{BC} and r_{CA} . The C_9 coefficient is approximated by

$$C_9^{ABC} \approx - \sqrt{C_6^{AB} C_6^{AC} C_6^{BC}} \quad (3.17)$$

The three-body contribution has a small effect on medium-sized molecules and is damped according to equation (3.16). The damping function $f_{d,(3)}(\bar{r}_{ABC})$ is similar to the one shown in equation (3.15) with \bar{r}_{ABC} being the geometric mean of r_{AB} , r_{BC} and r_{CA} . It can be used with both variants of the $E^{(2)}$ term, although the three-body term itself will always be calculated using the zero damping scheme. Adding the three-body correction has proven to give quite accurate results for the thermochemistry of supramolecular systems[280]. Note that the three-body term is included in D4 by default.

Basic Usage

The D3 correction can be invoked by the `!D3` keyword that will automatically make use of the default Becke-Johnson damping and is thus equivalent to `!D3BJ`. The zero damping scheme can be used with `!D3ZERO`. Note that the Becke-Johnson scheme is generally recommended.

```
!PBE D3
```

The three-body term can be invoked via the keyword `!ABC`.

```
!PBE D3 ABC
```

Note

Note that not all methods are parameterized for all damping options. E.g. Hartree-Fock (HF) is only parametrized with BJ-damping, while M06 is only parameterized with zero damping.

The more recent and generally recommended D4 correction can be used with the `!D4` keyword. Note that D4 uses Becke-Johnson damping and the three-body term by default.

```
!PBE D4
```

The D4 correction can also be defined in the `%method` block of the input:

```
! PBE def2-TZVP

%method
  DFTDOpt      5      # 5 = D4; 4 = D3 (BJ)
end
```

Custom parameters

If there is a functional for which parameters are known but not yet implemented into ORCA, they can be specified manually via the `%method` block.

Warning

Usage of custom parameters is at own risk and is generally not recommended. A list of some available parameters for D3 can be found at the [website of the Grimme group](#).

Important

GGA and hybrid functionals should only be used with $s_6 = 1.0$ to ensure asymptotically correct behavior. Double-hybrid functionals already account for parts of the dispersion interaction and should therefore be used with $s_6 < 1.0$.

For D3 with Becke-Johnson damping, the s_6 , a_1 , s_8 , and a_2 parameters can be adjusted:

```
!B2PLYP D3

%method
  D3S6 0.6400
  D3S8 0.9147
  D3A1 0.3065
```

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```
D3A2 5.0570
end
```

For D4, the s_9 parameter of the three-body term can be adjusted as well.

```
!B2PLYP D4

%method
D4S6 0.6400
D4S8 1.1689
D4A1 0.4415
D4A2 4.7311
D4S9 1.0000
end
```

For the D3 variant with zero damping the parameters s_6 , rs_6 , s_8 , and α_6 can be adjusted.

```
!BLYP D3ZERO

%method
D3S6      1.000
D3RS6     1.094
D3S8      1.682
D3alpha6  14
end
```

For some functionals, there are also special parameters, which were optimized for use with the def2-TZVPP triple-zeta basis set. This option is only available with zero damping and can be invoked by the keywords !D3ZERO D3TZ. Preliminary results in the SI of Ref. [272] indicate that results are only slightly worse than with quadruple-zeta basis sets using the default parameters. This option should be carefully tested for future use in large computations.

Example

In this first example, the DFT-D4 dispersion correction is used.

```
!PBE def2-TZVP D4

* xyz 0 1
C      0.000000      0.000000      0.000000
O      0.000000      0.000000      1.400000
O      0.000000      0.000000     -1.400000
*
```

The output for the D4 dispersion correction in the ORCA output will look like this:

```
-----
                        DFT DISPERSION CORRECTION
                        DFTD4 V3.4.0
-----
```

The PBE functional is recognized

Active option DFTDOPT ... 5

```
-----
Dispersion correction      -0.000936618
-----
```

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```
FINAL SINGLE POINT ENERGY      -188.360452990031
-----
```

The total dispersion energy E_{disp} is given as the Dispersion correction and is automatically included in the final single point energy. As discussed above, the individual parameters may be adjusted manually.

```
!PBE def2-TZVP D4

%method
  D4S6 1.0
  D4A1 0.4289
  D4S8 0.7875
  D4A2 4.4407
  D4S9 0.9000
end

* xyz 0 1
  C      0.000000      0.000000      0.000000
  O      0.000000      0.000000      1.400000
  O      0.000000      0.000000     -1.400000
*
```

This results in the same output as above, but with additional messages that user inputs were found for the parameters:

```
A user input s6-coefficient scaling factor has been recognized
A user input a1-coefficient scaling factor has been recognized
A user input s8-coefficient scaling factor has been recognized
A user input a2-coefficient scaling factor has been recognized
A user input s9-coefficient scaling factor has been recognized
```

Keywords

Table 3.13: Simple input keywords for the DFT-D corrections.

Keyword	Description
D2	Activates D2 correction
D3	Activates D3 correction with BJ damping (D3(BJ))
D3BJ	Activates D3 correction with BJ damping (D3(BJ))
D3ZERO	Activates D3 correction with zero damping (D3(0))
D30	Activates D3 correction with zero damping (D3(0)), equivalent to D3ZERO
D3TZ	Activates special triple- ζ D3 parameterization (only with D3ZERO)
D4	Activates D4 correction (BJ and ATM included)
ABC	Activates three-body term
ATM	Activates three-body term, equivalent to ABC
NOVDW	Deactivates DFT-D dispersion corrections

Table 3.14: %method block input keywords for the DFT-D corrections.

Keyword	Options	Description
DFTDOPT	1	Activate the original D correction[281] (deprecated)
	2	Activate the D2 correction (deprecated)
	3	Activate the D3ZERO correction
	4	Activate the D3BJ correction
	5	Activate the D4 correction
D3S6	<real>	Controls s_6 parameter for D3
D3S8	<real>	Controls s_8 parameter for D3
D3A1	<real>	Controls a_1 parameter for D3
D3A2	<real>	Controls a_2 parameter for D3
D3RS6	<real>	Controls rs_6 parameter for zero damping
D3alpha6	<real>	Controls α_6 parameter for zero damping
D4S6	<real>	Controls s_6 parameter for D4
D4S8	<real>	Controls s_8 parameter for D4
D4A1	<real>	Controls a_1 parameter for D4
D4A2	<real>	Controls a_2 parameter for D4
D4S9	<real>	Controls s_9 parameter of ABC term for D4
DFTDScaleC6	<real>	Defines the C6 scaling coefficient

Available Parameters

Table 3.15: DFT-D4 (!D4) parameters used for various functionals.

Functional	s_6	s_8	a_1	a_2	s_9
HF	1.0000	1.61679827	0.44959224	3.35743605	1.0000
BLYP	1.0000	2.34076671	0.44488865	4.09330090	1.0000
BPBE	1.0000	3.64405246	0.52905620	4.11311891	1.0000
BP86	1.0000	3.35497927	0.43645861	4.92406854	1.0000
BPW91	1.0000	3.24571506	0.50050454	4.12346483	1.0000
GLYP	1.0000	4.23798924	0.38426465	4.38412863	1.0000
LB94	1.0000	2.59538499	0.42088944	3.28193223	1.0000
mPWLYP	1.0000	1.25842942	0.25773894	5.02319542	1.0000
mPWPW	1.0000	1.82596836	0.34526745	4.84620734	1.0000
OLYP	1.0000	2.74836820	0.60184498	2.53292167	1.0000
OPBE	1.0000	3.06917417	0.68267534	2.22849018	1.0000
PBE	1.0000	0.95948085	0.38574991	4.80688534	1.0000
RPBE	1.0000	1.31183787	0.46169493	3.15711757	1.0000
REVPBE	1.0000	1.74676530	0.53634900	3.07261485	1.0000
PW86PBE	1.0000	1.21362856	0.40510366	4.66737724	1.0000
RPW86PBE	1.0000	1.12624034	0.38151218	4.75480472	1.0000
PW91	1.0000	0.77283111	0.39581542	4.93405761	1.0000
PW91P86	1.0000	0.32801227	0.35874687	6.05861168	1.0000
XLYP	1.0000	1.62972054	0.11268673	5.40786417	1.0000
B97BECKE	1.0000	0.87854260	0.29319126	4.51647719	1.0000
TPSS	1.0000	1.76596355	0.42822303	4.54257102	1.0000
revTPSS	1.0000	1.53089454	0.44880597	4.64042317	1.0000
SCAN	1.0000	1.46126056	0.62930855	6.31284039	1.0000
B1LYP	1.0000	1.98553711	0.39309040	4.55465145	1.0000
B3LYP	1.0000	2.02929367	0.40868035	4.53807137	1.0000
BHANDHLYP	1.0000	1.65281646	0.27263660	5.48634586	1.0000

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Table 3.15 – continued from previous page

Functional	s_6	s_8	a_1	a_2	s_9
B1P	1.0000	3.36115015	0.48665293	5.05219572	1.0000
B3P86	1.0000	3.08822155	0.47324238	4.98682134	1.0000
B1PW91	1.0000	3.02227550	0.47396846	4.49845309	1.0000
B3PW91	1.0000	2.88364295	0.46990860	4.51641422	1.0000
O3LYP	1.0000	1.75762508	0.10348980	6.16233282	1.0000
REVPBE0	1.0000	1.57185414	0.38705966	4.11028876	1.0000
REVPBE38	1.0000	1.66597472	0.39476833	4.39026628	1.0000
PBE0	1.0000	1.20065498	0.40085597	5.02928789	1.0000
PWP1	1.0000	0.60492565	0.46855837	5.76921413	1.0000
PW1PW	1.0000	0.96850170	0.42427511	5.02060636	1.0000
mPW1PW	1.0000	1.80841716	0.42961819	4.68892341	1.0000
mPW1LYP	1.0000	1.15591153	0.25603493	5.32083895	1.0000
PW6B95	1.0000	-0.31926054	0.04142919	5.84655608	1.0000
TPSSh	1.0000	1.85897750	0.44286966	4.60230534	1.0000
TPSS0	1.0000	1.62438102	0.40329022	4.80537871	1.0000
X3LYP	1.0000	1.54701429	0.20318443	5.61852648	1.0000
M06L	1.0000	0.59493760	0.71422359	6.35314182	1.0000
M06	1.0000	0.16366729	0.53456413	6.06192174	1.0000
wB97	1.0000	6.55792598	0.76666802	8.36027334	1.0000
wB97X	1.0000	-0.07519516	0.45094893	6.78425255	1.0000
B97M-D4	1.0000	0.66330000	0.42880000	3.99350000	1.0000
CAM-B3LYP	1.0000	1.66041301	0.40267156	5.17432195	1.0000
LC-BLYP	1.0000	1.60344180	0.45769839	7.86924893	1.0000
B2PLYP	0.6400	1.16888646	0.44154604	4.73114642	1.0000
B2GP-PLYP	0.5600	0.94633372	0.42907301	5.18802602	1.0000
mPW2PLYP	0.7500	0.45788846	0.42997704	5.07650682	1.0000
PWPB95	0.8200	-0.34639127	0.41080636	3.83878274	1.0000
B97-D	1.0000	1.69460052	0.28904684	4.13407323	1.0000
RSCAN	1.0000	0.87728975	0.49116966	5.75859346	1.0000
r2SCAN	1.0000	0.60187490	0.51559235	5.77342911	1.0000
r2SCANh	1.0000	0.83240000	0.49440000	5.90190000	1.0000
r2SCAN0	1.0000	0.89920000	0.47780000	5.87790000	1.0000
r2SCAN50	1.0000	1.04710000	0.45740000	5.89690000	1.0000
wB97X-D4rev	1.0000	0.44850000	0.33060000	4.27900000	1.0000
wB97M-D4rev	1.0000	0.84200000	0.35900000	4.66800000	1.0000
wR2SCAN	1.0000	1.00000000	0.38340000	5.78890000	1.0000
r2SCAN0-DH	0.9424	0.38560000	0.42710000	5.85650000	1.0000
r2SCAN-CIDH	0.8666	0.53360000	0.41710000	5.91250000	1.0000
r2SCAN-QIDH	0.7867	0.29550000	0.40010000	5.83000000	1.0000
r2SCAN0-2	0.7386	0.00000000	0.40300000	5.51420000	1.0000
Pr2SCAN50	0.7964	0.34210000	0.46630000	5.79160000	1.0000
kPr2SCAN50	0.8402	0.12120000	0.43820000	5.82320000	1.0000
wPr2SCAN50	0.8143	0.38420000	0.41350000	5.87730000	1.0000
Pr2SCAN69	0.7167	0.00000000	0.46440000	5.25630000	1.0000
revDSD-PBEP86/2021	0.5917	0.00000000	0.37100000	4.20140000	1.0000
revDOD-PBEP86/2021	0.6158	0.00000000	0.34400000	4.24270000	1.0000
LRC-PBE	1.0000	1.17000000	0.37800000	4.81600000	1.0000

Table 3.16: DFT-D3(BJ) (!D3BJ) parameters used for various functionals.

Functional	s_6	s_8	a_1	a_2	s_9
HF	1.0000	0.91710000	0.33850000	2.88300000	1.0000
BP86	1.0000	3.28220000	0.39460000	4.85160000	1.0000

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Table 3.16 – continued from previous page

Functional	s_6	s_8	a_1	a_2	s_9
BLYP	1.0000	2.69960000	0.42980000	4.23590000	1.0000
REVPBE	1.0000	2.35500000	0.52380000	3.50160000	1.0000
B97-D	1.0000	2.26090000	0.55450000	3.22970000	1.0000
PBE	1.0000	0.78750000	0.42890000	4.44070000	1.0000
RPBE	1.0000	0.83180000	0.18200000	4.00940000	1.0000
RPW86PBE	1.0000	1.38450000	0.46130000	4.50620000	1.0000
B3LYP	1.0000	1.98890000	0.39810000	4.42110000	1.0000
BHANDHLYP	1.0000	1.03540000	0.27930000	4.96150000	1.0000
TPSS	1.0000	1.94350000	0.45350000	4.47520000	1.0000
TPSS0	1.0000	1.25760000	0.37680000	4.58650000	1.0000
PBE0	1.0000	1.21770000	0.41450000	4.85930000	1.0000
REVPBE38	1.0000	1.47600000	0.43090000	3.94460000	1.0000
PW6B95	1.0000	0.72570000	0.20760000	6.37500000	1.0000
B2PLYP	0.6400	0.91470000	0.30650000	5.05700000	1.0000
mPWLYP	1.0000	2.00770000	0.48310000	4.53230000	1.0000
OLYP	1.0000	2.62050000	0.52990000	2.80650000	1.0000
BPBE	1.0000	4.07280000	0.45670000	4.39080000	1.0000
OPBE	1.0000	3.38160000	0.55120000	2.94440000	1.0000
B3PW91	1.0000	2.85240000	0.43120000	4.46930000	1.0000
REVPBE0	1.0000	1.75880000	0.46790000	3.76190000	1.0000
TPSSh	1.0000	2.23820000	0.45290000	4.65500000	1.0000
CAM-B3LYP	1.0000	2.06740000	0.37080000	5.47430000	1.0000
B2GP-PLYP	0.5600	0.25970000	0.00000000	6.33320000	1.0000
PWPB95	0.8200	0.29040000	0.00000000	7.31410000	1.0000
SCAN	1.0000	0.00000000	0.53800000	5.42000000	1.0000
RSCAN	1.0000	1.08860000	0.47020000	5.73410000	1.0000
R2SCAN	1.0000	0.78980000	0.49480000	5.73080000	1.0000
R2SCANh	1.0000	1.12360000	0.47090000	5.91570000	1.0000
R2SCAN0	1.0000	1.18460000	0.45340000	5.89720000	1.0000
R2SCAN50	1.0000	1.32940000	0.43110000	5.92400000	1.0000
WR2SCAN	1.0000	1.00000000	0.38340000	5.78890000	1.0000
r2SCAN0-DH	0.9424	0.38560000	0.42710000	5.85650000	1.0000
r2SCAN-CIDH	0.8666	0.53360000	0.41710000	5.91250000	1.0000
r2SCAN-QIDH	0.7867	0.29550000	0.40010000	5.83000000	1.0000
r2SCAN0-2	0.7386	0.00000000	0.40300000	5.51420000	1.0000
Pr2SCAN50	0.7964	0.34210000	0.46630000	5.79160000	1.0000
kPr2SCAN50	0.8402	0.12120000	0.43820000	5.82320000	1.0000
wPr2SCAN50	0.8143	0.38420000	0.41350000	5.87730000	1.0000
Pr2SCAN69	0.7167	0.00000000	0.46440000	5.25630000	1.0000
revDSD-PBEP86/2021	0.5917	0.00000000	0.37100000	4.20140000	1.0000
revDOD-PBEP86/2021	0.6158	0.00000000	0.34400000	4.24270000	1.0000
DSD-BLYP	0.5000	0.21300000	0.00000000	6.05200000	1.0000
DSD-BLYP/2013	0.5700	0.00000000	0.00000000	5.40000000	1.0000
DSD-PBEB95	0.6100	0.00000000	0.00000000	6.20000000	1.0000
DSD-PBEP86	0.4180	0.00000000	0.00000000	5.65000000	1.0000
DSD-PBEP86/2013	0.4800	0.00000000	0.00000000	5.60000000	1.0000
B97M-D3BJ	1.0000	0.13840000	-0.07800000	5.59460000	1.0000
wB97X-D3BJ	1.0000	0.26410000	0.00000000	5.49590000	1.0000
wB97M-D3BJ	1.0000	0.39080000	0.56600000	3.12800000	1.0000
wB97X-2	0.5470	0.00000000	3.52000000	7.79500000	1.0000
PBE0DH	0.8800	1.08900000	0.00000000	6.38500000	1.0000
PBE02	0.5400	0.51500000	0.00000000	8.34500000	1.0000
PBE-QIDH	0.6100	0.56600000	0.11400000	7.53800000	1.0000