MANUAL

Minnesota Functional Module

Version 5.0

Subroutines for evaluating the following exchange-correlation functionals: GAM, M05, M05-2X, M06, M06-2X, M06-HF, M06-L, M08-HX, M08-SO, M11, M11-L, MN12-L, MN12-SX, MN15, MN15-L, N12, N12-SX, revM06, revM06-L, revM11, M06-SX, SOGGA, SOGGA11, and SOGGA11-X

Documentation

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Contents

Licensing

Executive summary

Minnesota Functional Module (abbreviated *MFM*) is a Fortran77 code for evaluating the GAM, M05, M05-2X, M06, M06-2X, M06-HF, M06-L, M08-HX, M08-SO, M11, M11-L, MN12-L, MN12-SX, MN15, MN15-L, N12, N12-SX, revM06, revM06-L, revM11, M06-SX, SOGGA, SOGGA11, and SOGGA11-X exchange-correlation functionals for Kohn-Sham density functional theory. The subroutines are in the accompanying tar file.

Literature references

A. Original references for functionals

GAM

Yu, H. S.; Zhang, W.; Verma, P.; He, X.; Truhlar, D. G. *Phys. Chem. Chem. Phys*. **2015**, 17, 12146-12160. doi.org/10.1039/C5CP01425E

M05

Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103. doi.org/10.1063/1.2126975

M05-2X

Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364-382. doi.org/10.1021/ct0502763

M06 and M06-2X

Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, 120, 215-241. doi.org/10.1007/s00214-007-0310-x
Erratum: **119**, 525 (2008). doi.org/10.1007/s00214-007-0401-8

M06-HF

Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, 110, 13126-13130. doi.org/10.1021/jp066479k

M06-L

Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101. doi.org/10.1063/1.4948728

M08-HX and M08-SO

Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2008**, *4*, 1849-1868.
doi.org/10.1021/ct800246v

M11

Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett*. **2011**, 2, 2810-2817.
doi.org/10.1021/jz201170d
Note that in eqs 21 and 22 of the M11 paper, *Y* should be *X*/100.

M11-L

Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett*. **2012**, 3, 117-124.
doi.org/10.1021/jz201525m

MN12-L

Peverati, R.; Truhlar, D. G. *Phys. Chem. Chem. Phys*. **2012**, 14, 13171-13174.
doi.org/10.1039/c2cp42025b

MN12-SX and N12-SX

Peverati, R.; Truhlar, D. G. *Phys. Chem. Chem. Phys*. **2012**, 14, 16187-16191.
doi.org/10.1039/C2CP42576A

MN15

Yu, H. S.; He, X.; Li, S.; Truhlar, D. G. *Chem. Sci.* **2016**, 7, 50325051.
doi.org/10.1039/C6SC00705h
Correction: **7**, 6278-6279 (2016). doi.org/10.1039/c6sc90044e

MN15-L

Yu, H. S.; He, X.; Truhlar, D. G. *J. Chem. Theory Comput*. **2016**, 12, 1280-1293.
doi.org/10.1021/acs.jctc.5b01082

N12

Peverati, R.; Truhlar, D. G. *J. Chem. Theory Comput.* **2012**, 8, 2310-12319.
doi.org/10.1021/ct3002656

revM06

Wang, Y.; Verma, P.; Jin, X. S.; Truhlar, D. G.; He, X. *Proc. Natl. Acad. Sci. U.S.A.* **2018** 115, 10257-10262**.**
doi.org/10.1073/pnas.1810421115

revM06-L

Wang, Y.; Jin, X. S.; Yu, H. S.; Truhlar, D. G.; He, X. *Proc. Natl. Acad. Sci. U.S.A.* **2017** 114, 8487-8492. doi.org/10.1073/pnas.1705670114

revM11

Verma, P.; Wang, Y.; Ghosh, S.; He, X.; Truhlar, D.G. *J. Phys. Chem. A*, **2019**, 123, 2966-2990. doi.org/10.1021/acs.jpca.8b11499

M06-SX

Wang, Y.; Verma, P.; Zhang, L. J.; Li, Y. Q.; Liu, Z. H.; Truhlar, D.G.; He, X., **2019**, submitted.

SOGGA

Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2008**, *128*, 184109. doi.org/10.1063/1.2912068

SOGGA11

Peverati, R.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2011**, *2*, 1911-1997. doi.org/10.1021/jz200616w

Note that there is a typo in eq. 3 of the SOGGA11 paper. The correct expression is:

$$g_1^x = \sum_{i=0}^{m} a_i^x \left(1 - \frac{1}{1 + \frac{\mu}{\kappa} s^2} \right)^i$$

SOGGA11-X

Peverati, R.; D. G. Truhlar, *J. Chem. Phys*. **2011**, 135, 191102. doi.org/10.1063/1.3663871

B. Reviews

Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res*. **2008**, 41, 157-167. doi.org/10.1021/ar700111a

Y. Zhao and D. G. Truhlar, Chemical Physics Letters 502, 1-13 (2011). doi.org/10.1016/j.cplett.2010.11.060

Input and output

INPUT:

RA, RB - Spin densities

D1RA, D1RB - Spin density gradients

TA, TB - τ_σ and τ_β

NGrid - total number of grid points at which the functional is evaluated.

OUTPUT:

F - Functional values on the grids

D1F - First derivatives with respect to RA, RB, GA, GB, TA, TB on the grids

Notes

1. We used Becke's definition (J. Chem. Phys. **104** 1040 (1996)) of τ_σ and τ_β. By this definition they are two times larger than spin kinetic energy densities.

2. The correlation part of all Minnesota functionals uses the local spin density part of the Perdew-Wang-91 correlation functional (J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244-13249 (1992)), which is a fit to the correlation energy of a uniform electron gas (lsdac subroutine). Since we are not allowed to distribute the work of others, **users should provide their own subroutine for this LSDA correlation functional**, or they may find help on Kieron Burke's web site at:
   http://www.chem.uci.edu/~kieron/dftold2/pubs/PBE.asc
   http://www.chem.uci.edu/~kieron/dftold2/pubs/PBEsol.html

3. The correlation part of all M08-class functionals also needs to use the $H(r_s,\zeta,t)$ function in the PBE correlation (PBEH0 subroutine). As for the previous point, we are not allowed to distribute this subroutine and **users should provide their own**, or they may find help on the author's (Kieron Burke) web site at:
   http://www.chem.uci.edu/~kieron/dftold2/pubs/PBE.asc
   http://www.chem.uci.edu/~kieron/dftold2/pubs/PBEsol.html

4. The correlation parts of the N12, GAM, and N12-SX are obtained from B97-like expansion truncated at the fourth order, with the opposite spin contribution calculated as:

$$E_{c\alpha\beta} = \int d\mathbf{r}\varepsilon_{c\alpha\beta}^{\mathrm{UEG}} \left\{ \sum_{i=0}^{n} b_i u_{c\alpha\beta}^{i} \right\}$$

and the same spin contribution calculated as:

$$E_{c\sigma\sigma} = \int d\mathbf{r}\varepsilon_{c\sigma\sigma}^{\mathrm{UEG}} \left\{ \sum_{i=0}^{n'} c_i u_{c\sigma\sigma}^{i} \right\}$$

once again, **users should provide their own subroutine for this**, and use the parameters in Table 1. Note that there is a typo in the N12 paper, the corrected values for b_i and c_i have been showed below.

Table 1. Parameters of the B97-like expansion for the N12, GAM, and N12-SX correlation functionals.

	12	AM	12-SX
b_0	1.00000D+00	0.860548D+00	2.63373D+00
b_1	3.24511D+00	-2.94135D+00	-1.05450D+00
b_2	-2.52893D+01	15.4176D+00	-7.29853D-01
b_3	1.44407D+01	-5.99825D+00	4.94024D+00
b_4	1.96870D+01	-23.4119D+00	-7.31760D+00
c_0	1.00000D+00	0.231765D+00	8.33615D-01
c_1	-5.53170D+00	0.575592D+00	3.24128D+00
c_2	3.07958D+01	-3.43391D+00	-1.06407D+01
c_3	-5.64196D+01	5.77281D+00	-1.60471D+01
c_4	3.21250D+01	9.52449D+00	2.51047D+01

5. One needs to add a portion of the Hartree-Fock exchange energy to the total exchange-correlation energy for the M05, M05-2X, M06, M06-2X, M06-HF, M08-HX, M08-SO, SOGGA11-X, MN15, revM06, and revM11 functionals. See the details in Table 2.

6. The exchange part of M11 and rev M11 requires range-separation with the error function with

M11: 42.8% short-range HF exchange, and 100% long-range HF exchange.

The range parameter ω is 0.225 a_0^{-1}.

revM11: 22.5% short-range HF exchange and 100% long-range exchange.

The range parameter ω is 0.40 a_0^{-1}.

7. The exchange part of N12-SX and MN12-SX requires 25% of "screened exchange", which is: 25% short-range HF exchange and 0% long-range HF exchange. The range parameter μ is 0.11.
8. The exchange part of M06-SX requires 33.5% of "screened exchange", which is: 33.5% short-range HF exchange and 0% long-range HF exchange. The range parameter μ is 0.10.

Table 2. Hartree-Fock exchange energies in the Minnesota functionals[a]

Functional	Fraction of Hartree-Fock exchange energy
M05	$0.28E^{\mathrm{HFE}}$
M05-2X	$0.56E^{\mathrm{HFE}}$
M06	$0.27E^{\mathrm{HFE}}$
M06-2X	$0.54E^{\mathrm{HFE}}$
M06-HF	$1.0E^{\mathrm{HFE}}$
M08-HX	$0.5223E^{\mathrm{HFE}}$
M08-SO	$0.5679E^{\mathrm{HFE}}$
M11	$0.428E^{\mathrm{SR\text{-}HFE}} + 1.0E^{\mathrm{LR\text{-}HFE}}$ ($\omega = 0.25$)
N12-SX, MN12-SX	$0.25E^{\mathrm{SX}}$ ($\mu = 0.11$)
SOGGA, SOGGA11, M06-L,	0
MN15	$0.44\ E^{\mathrm{HFE}}$
SOGGA11-X	$0.4015E^{\mathrm{HFE}}$
revM06	$0.4041E^{\mathrm{HFE}}$
revM11	$0.225E^{\mathrm{SR\text{-}HFE}} + 1.0E^{\mathrm{LR\text{-}HFE}}$ ($\omega = 0.40$)
M06-SX	$0.335E^{\mathrm{SX}}$ ($\mu = 0.10$)

[a] E^{HFE} is the Hartree-Fock exchange energy, $E^{\mathrm{SR\text{-}HFE}}$ and $E^{\mathrm{LR\text{-}HFE}}$ are the short-range and long-range Hartree–Fock exchange energies respectively, and E^{SX} is the short-range Hartree–Fock screened exchange in a screened functional

Reference energies and gradients

Table 3 and 4 present reference energies and forces of CH_3 (open shell, doublet) and H_2O (closed shell, singlet) with the 6-31+G** basis set and a pruned (99,590) grid.

Geometries of CH_3 (in angstrom)

****

C	0.000000	0.000000	0.000000
H	0.000000	1.078000	0.000000
H	0.933000	-0.539000	0.000000
H	-0.933000	-0.539000	0.000000

****

Table 3. Reference energies (E_h) and forces (X,Y,Z, E_h/a_0) for CH_3

PW6B95	E=	-39.888691		
	C	0.000000	0.000294	0.000000
	H	0.000000	0.000371	0.000000
	H	0.000665	-0.000333	0.000000
	H	-0.000665	-0.000333	0.000000
PWB6K	E=	-39.854636		
	C	0.000000	0.000294	0.000000
	H	0.000000	-0.002977	0.000000
	H	-0.002231	0.001342	0.000000
	H	0.002231	0.001342	0.000000
SOGGA	E=	-39.538835		
	C	0.000000	0.000313	0.000000
	H	0.000000	0.011083	0.000000
	H	0.009947	-0.005698	0.000000
	H	-0.009947	-0.005698	0.000000
SOGGA11	E=	-39.842525		
	C	0.000000	0.000229	0.000000
	H	0.000000	0.006611	0.000000
	H	0.006004	-0.003420	0.000000
	H	-0.006004	-0.003420	0.000000
SOGGA11-X	E=	-39.831323		
	C	0.000000	0.000292	0.000000
	H	0.000000	0.003387	0.000000

	H	0.003276	-0.001840	0.000000
	H	-0.003276	-0.001840	0.000000
N12	E=	-39.822945		
	C	0.000000	0.000149	0.000000
	H	0.000000	-0.000495	0.000000
	H	-0.000108	0.000173	0.000000
	H	0.000108	0.000173	0.000000
N12-SX	E=	-39.823220		
	C	0.000000	0.000282	0.000000
	H	0.000000	-0.002663	0.000000
	H	-0.001970	0.001191	0.000000
	H	0.001970	0.001191	0.000000
M08-HX	E=	-39.828570		
	C	0.000000	0.000294	0.000000
	H	0.000000	0.003959	0.000000
	H	0.003782	-0.002126	0.000000
	H	-0.003782	-0.002126	0.000000
M11	E=	-39.805603		
	C	0.000000	0.000277	0.000000
	H	0.000000	0.005260	0.000000
	H	0.004876	-0.002769	0.000000
	H	-0.004876	-0.002769	0.000000
M11-L	E=	-39.827503		
	C	0.000000	0.000257	0.000000
	H	0.000000	0.004995	0.000000
	H	0.004663	-0.002626	0.000000
	H	-0.004663	-0.002626	0.000000
MN12-L	E=	-39.776262		
	C	0.000000	0.000205	0.000000
	H	0.000000	0.001150	0.000000
	H	0.001371	-0.000678	0.000000
	H	0.001371	-0.000678	0.000000
MN12-SX	E=	-39.802089		
	C	0.000000	0.000233	0.000000
	H	0.000000	0.001712	0.000000
	H	0.001846	-0.000972	0.000000
	H	-0.001846	-0.000972	0.000000
GAM	E=	-39.857257		

	C	0.000000	0.000306	0.000000
	H	0.000000	0.000744	0.000000
	H	0.000994	-0.000525	0.000000
	H	-0.000994	-0.000525	0.000000
MN15-L	E=	-39.790513		
	C	0.000000	0.000313	0.000000
	H	0.000000	0.008751	0.000000
	H	0.007937	-0.004532	0.000000
	H	-0.007937	-0.004532	0.000000
MN15	E=	-39.780507		
	C	0.000000	0.000300	0.000000
	H	0.000000	0.001890	0.000000
	H	0.001985	-0.001095	0.000000
	H	-0.001985	-0.001095	0.000000
revM06-L	E=	-39.811321		
	C	0.000000	0.000292	0.000000
	H	0.000000	0.002164	0.000000
	H	0.002219	-0.001228	0.000000
	H	-0.002219	-0.001228	0.000000
revM06	E=	-39.797379		
	C	0.000000	0.000296	0.000000
	H	0.000000	0.002391	0.000000
	H	0.002418	-0.001343	0.000000
	H	-0.002418	-0.001343	0.000000
revM11	E=	-39.809756		
	C	0.000000	0.000300	0.000000
	H	0.000000	0.003959	0.000000
	H	0.003774	-0.002130	0.000000
	H	-0.003774	-0.002130	0.000000
M06-SX	E=	-39.744493		
	C	0.000000	0.000295	0.000000
	H	0.000000	0.001151	0.000000
	H	0.001343	-0.000723	0.000000
	H	-0.001343	-0.000723	0.000000
PBEsol	E=	-39.586795		
	C	0.000000	0.000311	0.000000
	H	0.000000	0.010513	0.000000
	H	0.009453	-0.005412	0.000000
	H	-0.009453	-0.005412	0.000000

WC06	E=	-39.673096		
	C	0.000000	0.000307	0.000000
	H	0.000000	0.008746	0.000000
	H	0.007921	-0.004527	0.000000
	H	-0.007921	-0.004527	0.000000
RPBE	E=	-39.847464		
	C	0.000000	0.000305	0.000000
	H	0.000000	0.008991	0.000000
	H	0.008133	-0.004648	0.000000
	H	-0.008133	-0.004648	0.000000
revPBE	E=	-39.831098		
	C	0.000000	0.000305	0.000000
	H	0.000000	0.008874	0.000000
	H	0.008032	-0.004590	0.000000
	H	-0.008032	-0.004590	0.000000
B97-3	E=	-39.833716		
	C	0.000000	0.000300	0.000000
	H	0.000000	0.002450	0.000000
	H	0.002469	-0.001375	0.000000
	H	-0.002469	-0.001375	0.000000

Geometries of H_2O (in Å)

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O	0.000000	0.000000	0.000000
H	0.000000	0.000000	0.956914
H	0.926363	0.000000	-0.239868

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Table 4. Reference energies (E_h) and forces (X,Y,Z, E_h/a_0) for H_2O

M06	E=	-76.397702		
	O	-0.002239	0.000000	-0.001733
	H	-0.002242	0.000000	0.005209
	H	0.004481	0.000000	-0.003476
M06-L	E=	-76.420152		
	O	-0.002994	0.000000	-0.002317
	H	-0.000683	0.000000	0.003975
	H	0.003677	0.000000	-0.001658
M06-2X	E=	-76.394863		
	O	-0.002361	0.000000	-0.001828
	H	-0.002678	0.000000	0.005899
	H	0.005039	0.000000	-0.004072
M06-HF	E=	-76.391767		
	O	0.000348	0.000000	0.000270
	H	-0.005141	0.000000	0.006282
	H	0.004793	0.000000	-0.006551
M05-2X	E=	-76.416245		
	O	-0.000061	0.000000	-0.000047
	H	-0.002966	0.000000	0.003895
	H	0.003027	0.000000	-0.003848
M05	E=	-76.398883		
	O	-0.001497	0.000000	-0.001159
	H	-0.001588	0.000000	0.003598
	H	0.003085	0.000000	-0.002439
M08-HX	E=	-76.397793		
	O	-0.000086	0.000000	-0.000067
	H	-0.003293	0.000000	0.004343
	H	0.003379	0.000000	-0.004276

M08-SO	E=	-76.381535		
	O	-0.005417	0.000000	-0.004193
	H	-0.003612	0.000000	0.010262
	H	0.009029	0.000000	-0.006069
M11	E=	-76.403933		
	O	-0.001641	0.000000	-0.001270
	H	-0.003892	0.000000	0.006723
	H	0.005533	0.000000	-0.005453
M11-L	E=	-76.404506		
	O	0.003288	0.000000	0.002545
	H	-0.000043	0.000000	-0.003341
	H	-0.003245	0.000000	0.000795
MN12-L	E=	-76.355836		
	O	0.001127	0.000000	0.000873
	H	-0.003229	0.000000	0.003006
	H	0.002101	0.000000	-0.003879
MN12-SX	E=	-76.373687		
	O	-0.003107	0.000000	-0.002405
	H	-0.003170	0.000000	0.007304
	H	0.006277	0.000000	-0.004900
SOGGA11	E=	-76.423371		
	O	-0.003780	0.000000	-0.002926
	H	-0.000816	0.000000	0.004959
	H	0.004596	0.000000	-0.002033
SOGGA11-X	E=	-76.405420		
	O	-0.000473	0.000000	-0.000366
	H	-0.001773	0.000000	0.002779
	H	0.002246	0.000000	-0.002413
N12	E=	-76.383122		
	O	0.003850	0.000000	0.002980
	H	-0.002507	0.000000	-0.000738
	H	-0.001343	0.000000	-0.002242
N12-SX	E=	-76.385858		
	O	0.003032	0.000000	0.002347
	H	-0.003636	0.000000	0.001566
	H	0.000604	0.000000	-0.003913
GAM	E=	-76.402043		

	O	0.003354	0.000000	0.002596
	H	-0.000553	0.000000	-0.002749
	H	-0.002800	0.000000	0.000154
MN15-L	E=	-76.347439		
	O	-0.006624	0.000000	-0.005128
	H	-0.000844	0.000000	0.007933
	H	0.007468	0.000000	-0.002805
MN15	E=	-76.351267		
	O	-0.005094	0.000000	-0.003943
	H	-0.003620	0.000000	0.009939
	H	0.008715	0.000000	-0.005996
revM06-L	E=	-76.396983		
	O	0.002221	0.000000	0.001719
	H	-0.000568	0.000000	-0.001561
	H	-0.001654	0.000000	-0.000158
revM06	E=	-76.387777		
	O	0.000368	0.000000	0.000285
	H	-0.002491	0.000000	0.002838
	H	0.002123	0.000000	-0.003123
revM11	E=	-76.400663		
	O	-0.004213	0.000000	-0.003261
	H	-0.003825	0.000000	0.009293
	H	0.008038	0.000000	-0.006032
M06-SX	E=	-76.352728		
	O	0.001748	0.000000	0.001353
	H	-0.001950	0.000000	0.000714
	H	0.000202	0.000000	-0.002067
M08-HX	E=	-76.132125		
Exchange-only with	O	-0.011250	0.000000	-0.008708
$0.5223E^{HFE}$ included	H	-0.003871	0.000000	0.016623
	H	0.015122	0.000000	-0.007915
M08-HX	E=	-72.106719		
Correlation and $0.5223E^{HFE}$	O	-0.101534	0.000000	-0.078592
only (no meta exchange)	H	-0.005570	0.000000	0.112079
	H	0.107104	0.000000	-0.033487
M08-HX	E=	-67.697943		
Correlation-only with	O	-0.234053	0.000000	-0.181167

no meta or HF exchange	H	-0.010609	0.000000	0.255477
	H	0.244661	0.000000	-0.074310

Note: the final three entries in the above table are for developers.

Version history

Version 1, December 31, 2008
Original version

Version 1.1, April 23, 2009
Added SOGGA

Version 1.2, May 14, 2009
Fixed some bugs, added reference energies and forces in the manual

Version 1.3, May 12, 2011
Added SOGGA11

Version 1.4 October 07, 2011
Fixed some bugs, added reference citation for SOGGA11.

Version 1.5 November 07, 2011
Added SOGGA11-X and M11

Version 1.6 December 05, 2011
Added M11-L, fixed some bugs

Version 1.7 April 18, 2012
Added N12, fixed some bugs

Version 1.8 September 05, 2012
Added MN12-L, N12-SX and MN12-SX, fixed some bugs

Version 2.0 January 27, 2016
Added GAM, MN15-L and MN15

Version 3.0 March 16, 2018
Added revM06-L and revM06

Version 4.0 December 1, 2018
Added revM11

Version 5.0 October 6, 2019
Added M06-SX