

Supporting Information for:

An improved and broadly accurate local approximation to the exchange-correlation density functional: The MN12-L functional for electronic structure calculations in chemistry and physics.

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to be published in *PCCP*

Date of final revision: August 30, 2012

This supporting information consists of a total of 16 pages, and it is organized as follows:

- Section I presents the subdatabases of BC345.
- Section II presents details of the calculation and results.
- Section III presents Fortran routines for the MN12-L functional.
- References

I. Databases

In this work we performed two modifications to our databases: (i) we expanded the ionization potentials (IPs) database to include transition metals, and (ii) we updated the basis set for the atomic energies database. Details of these modifications, as well as a brief introduction to all other databases (iii), and their subsets (iv), are presented below.

(i) IP21. Our previous ionization potential database (IP13/03¹⁻⁴) contains data from six atoms: C, S, O, P, Si and Cl, and seven molecules (SH, Cl₂, OH, O₂, PH, PH₂ and S₂). We update it here by adding seven IPs of transition metal atoms and one IP of a transition metal containing molecule (FeC at the ground state experimental equilibrium distance, $R_e = 1.596 \text{ \AA}$). The new database is called IP21, and is composed by two subsets, IP13/03 with main group atoms and molecules, and IPM8 with metal and metal containing molecule. Calculations on molecules involve separately optimized geometries from neutral and cations. The MG3S basis set⁴ is used for the IP13/03 subset, the cc-pVTZ-DK basis set of Petersen et al.⁵ was used for the seven atoms in IPM8, while for the calculations of the IP of FeC we used the SDD+2fg⁶ basis for Fe and the def2-QZVPP basis⁷ for C. The scalar relativistic effects are included in the calculations of the seven transition metal atomic IPs by using the Douglas-Kroll-Hess (DKH) second-order

scalar relativistic Hamiltonian,⁸⁻¹⁰ while they are included in the calculations of FeC within the SDD relativistic effective core potential.⁶ The reference data for the IP21 database are collected in Table S1.

Table S1. Reference data (kcal/mol) for the IP21 database.

IP13/03	Reference	IPM8	Reference
C	259.7	Cr	156.01
S	238.9	Cu	178.17
SH	238.9	FeC	173.71
Cl	299.1	Mo	163.71
Cl ₂	265.3	Pd	192.24
OH	299.1	Rh	172.11
O	313.9	Ru	169.86
O ₂	278.9	Zn	216.63
P	241.9		
PH	234.1		
PH ₂	226.3		
S ₂	216.0		
Si	187.9		

(ii) AE17. The MG3S basis set that we previously used for the atomic energies database (AE17^{11,12}) is not sufficiently close to the basis set limit because it does not include core-polarization function. While this is not an issue for the chemistry databases, for which only the valence effects are important since the core-polarization effects cancels out, in the calculation of the absolute atomic energies these effects can not be forgotten. For this reason we used in this work the cc-pwCV5Z basis set¹³ for H, He, and atoms from Be to Ne and from Al to Ar, while we used the cc-pCVQZ basis set¹⁴ for Li, Be, Na and Mg atoms.

(iii) Other Databases. Other databases from previous work have been used in the current training function, namely:

- MGAE109/11:^{1,15} 109 main group atomization energies, for which we used the MG3S basis set.⁴
- SRMBE12:¹⁶ 12 single-reference metal bond energies, for which we used the def2-TZVP basis set.^{17,18}
- MRBE10:¹⁶ 10 multi-reference bond energies, for which we used the def2-TZVP basis set.^{17,18}
- IsoL6:¹⁹ 6 isomerization energies of large organic molecules, for which we used the MG3SXP basis set.²⁰

- EA13/03:¹⁻⁴ 13 electron affinities, for which we used the MG3S basis set.⁴
- PA8:²¹ 8 proton affinities, for which we used the MG3S basis set.⁴
- ABDE4/05^{1,22,23} and ABDEL8:^{24,23} 4 and 8 alkyl bond dissociation reaction energies, for which we used the MG3S basis set.⁴
- HC7/11:²⁴ 7 hydrocarbons, for which we used the 6-311+G(2df,2p) basis set.²⁵
- π TC13:^{3,21,22} 13 π system thermochemistry, for which we used the MG3S basis set.⁴
- HTBH38/08^{1,26,27} and NHTBH38/08:^{1,26,27} 38 hydrogen-transfer and 38 non-hydrogen-transfer barrier heights, for which we used the MG3S basis set.⁴
- NCCE31/05:^{2,28-30} 31 noncovalent complexation energies, for which we used the MG3S basis set.⁴
- DC9/12:^{11,31} 9 difficult cases, for which we used the MG3S basis set.⁴
- SSLC18:^{32,33} 18 equilibrium lattice constants of solids, for which we used the m-6-311G* basis set.³⁴
- DG6:³¹ 6 geometries of diatomic molecules, for which we used the 6-311+G(2df,2p) basis set.²⁵
- SLC34:³⁵ 34 semiconductors lattice constants, for which we used the m-6-311G* basis set.³⁴
- SBG31:³⁵ 31 semiconductors band gaps, for which we used the m-6-311G* basis set.³⁴
- SSCE8:³³ 8 solid-state cohesive energies, for which we used the m-6-311G* basis set.³⁴
- MGBL20:³¹ 20 main group bond length, for which we used the 6-311+G(2df,2p) basis set.²⁵

(iv) Subsets. Some of the subdatabases used in this letter are composed of subsubdatabases, each one representing a particular class of compound or a class of properties (e.g., proton affinities of Schiff basis or barrier heights of nucleophilic substitutions). The performance on these subsets may be of interest to specialists who are considering the subsets that already have a presence in the literature. The subsets are:

*AE6:*³⁶ six atomization energies (from MGAE109/11).

*SB1AE97:*¹⁶ small-B1 atomization energies (from MGAE109/11).

*LB1AE12:*¹⁶ large-B1 atomization energies (from MGAE109/11).

*TMBE15:*³⁵ 15 transition metals bond energies (from SRMBE13 and MRBE10).

*MBE18:*³⁵ 18 metals bond energies (from SRMBE13 and MRBE10).

*IP13/03:*¹⁻⁴ 13 ionization potentials of main group atoms and molecules (from IP21).

IPM8: 8 ionization potentials of metal atoms and metal containing molecule (from IP21).

π IE3/06:^{21,37} three π systems isomerization energies (from π TC13).

*PA-CP5/06:*²¹ five proton affinities of conjugated polyenes (from π TC13).

*PA-SB5/06:*²¹ five proton affinities of Schiff basis (from π TC13).

- HATBH12/08*:²⁷ 12 barrier heights of heavy-atom transfer (from NHTBH38/08).
NSBH16/08:²⁷ 16 barrier heights of nucleophilic substitution (from NHTBH38/08).
UABH10/08:²⁷ ten barrier heights of unimolecular and association reactions (from NHTBH38/08).
DBH24/08:³⁸ 24 diverse barrier heights (from HTBH38/08 and NHTBH38/08)
HB6/04:²⁸ six hydrogen bonding complexes (from NCCE31/05).
CT7/04:²⁸ seven charge-transfer complexes (from NCCE31/05).
DI6/04:²⁸ six dipole interaction complexes (from NCCE31/05).
WI7/05:^{2,28} seven weak interactions complexation energies (from NCCE31/05).
PPS5/05:^{2,28-30} five π - π stackings energies (from NCCE31/05).

Performances of MN12-L and all other considered functionals for the subsets are reported in the next section of this supporting information.

II. Details of the Calculations and Results

For the calculation of the mean unsigned error per bond (MUE_{PB}) of the atomization energies databases we used the following formula:

$$MUE_{PB} = \frac{1}{n_{\text{bond}}} \sum_{i=1}^{n_{\text{molec}}} \frac{|AE_i - AE_i^{\text{Ref}}|}{n_{\text{molec}}} \quad (\text{S1})$$

where n_{molec} is the total number of molecules in the database, AE_i and AE_i^{Ref} are respectively the calculated and the reference atomization energy for molecule i , and n_{bond} is the average number of bonds per molecule in the database, namely:

$$\begin{aligned} n_{\text{bond}} &= 4.71 \text{ for MGAE109/11,} \\ n_{\text{bond}} &= 5.10 \text{ for SB1AE97,} \\ n_{\text{bond}} &= 1.33 \text{ for LB1AE12,} \\ n_{\text{bond}} &= 4.67 \text{ for AE6,} \\ n_{\text{bond}} &= 9.22 \text{ for DC9/12.} \end{aligned} \quad (\text{S2})$$

The global mean unsigned error for BC345 is calculated from the databases as:

$$\begin{aligned} MUE(\text{BC345}) &= 1/n_{\text{tot}} \{ 109 * MUE_{PB}(\text{MGAE109/11}) + 13 * MUE(\text{SRMBE13}) + \\ &10 * MUE(\text{MRBE10}) + 6 * MUE(\text{IsoL6/11}) + \\ &21 * MUE(\text{IP21}) + 13 * MUE(\text{EA13/03}) + 8 * MUE(\text{PA8/06}) + \end{aligned}$$

$$4 * \text{MUE}(\text{ABDE4/05}) + 8 * \text{MUE}(\text{ABDEL8}) + 7 * \text{MUE}(\text{HC7/11}) + \\
 13 * \text{MUE}(\pi\text{TC13}) + 38 * \text{MUE}(\text{HTBH38/08}) + 38 * \text{MUE}(\text{NHTBH38/08}) + \\
 31 * \text{MUE}(\text{NCCE31/05}) + 9 * \text{MUE}(\text{DC9/12}) + 17 * \text{MUE}(\text{AE17}) \} \quad (\text{S3})$$

where n_{tot} is the total number of elements in the database (which is $n_{\text{tot}}=345$). The mean unsigned error for BC328xAE are calculated using the same formula, and excluding MUE(AE17) (with $n_{\text{tot}}=328$).

Detailed performances of MN12-L for BC345 and its subsets are presented in Table S2, and results for the significant subsets are reported in Table S3.

Table S2. Mean Unsigned Errors, Mean Signed Errors, Largest Absolute Error, and Smallest Absolute Error (all in kcal/mol) of the MN12-L Functional for Subsets of BC345.

MN12-L	MUE	MSE	Largest $ \epsilon $	Smallest $ \epsilon $
MGAE109/11	3.25	-0.71	17.50	0.02
per bond	0.69	-0.15		
SRMBE13	3.95	1.89	11.08	0.47
MRBE10	7.12	-1.18	24.67	0.29
IsoL6/11	1.07	-0.53	1.74	0.12
IP21	3.54	0.15	8.86	0.28
EA13/03	2.42	-2.28	11.82	0.00
PA8/06	1.91	-0.51	3.84	0.09
ABDE4/05	4.25	-1.70	6.63	2.07
ABDEL8	5.16	-5.16	19.03	0.10
HC7/11	2.58	0.00	3.86	0.14
π TC13	5.61	5.61	11.01	0.31
HTBH38/08	1.31	-0.32	4.91	0.11
NHTBH38/08	2.24	-1.69	9.53	0.06
NCCE31/05	0.46	-0.10	1.91	0.00
DC9/12	15.21	13.74	56.60	0.39
per bond	1.65	1.49		
AE17	9.73	-3.41	24.99	1.10

Table S3. Mean Unsigned Errors of the MN12-L Functional Compared to Those of Other Functionals for Subsets of the BC345 Database

Functional:	PBE	SOGGA	PBEsol	SOGGA11	N12	HSE	TPSS	revTPSS	M06-L	M11-L	MN12-L
AE6 ^a	3.16	7.53	7.45	1.78	0.91	0.94	1.02	1.17	0.64	1.00	0.65
SB1AE97 ^a	2.77	7.36	7.51	1.47	1.12	0.82	0.99	0.85	0.83	0.68	0.63
LB1AE12 ^a	12.98	23.27	22.67	8.38	6.03	2.81	3.70	4.13	2.25	2.94	2.72
TMBE15	9.62	14.96	14.53	11.67	5.47	14.99	7.58	8.06	7.74	4.43	5.26

MBE18	8.23	12.76	12.42	10.02	5.12	12.81	6.52	7.00	6.70	4.06	4.79
IP13	3.62	2.48	2.66	4.74	3.14	3.23	3.09	2.96	3.08	3.11	2.71
IPM8	10.58	8.46	10.95	8.81	12.85	5.43	6.00	5.63	5.04	6.96	4.90
π IE3/06	8.78	9.05	9.03	8.86	9.14	5.91	8.44	8.45	5.43	7.65	7.50
PA-CP5/06	4.34	1.64	1.91	5.23	7.63	5.89	8.57	8.67	7.94	4.79	4.14
PA-SB5/06	4.92	3.47	3.59	8.73	9.28	6.70	7.47	6.67	6.19	3.98	5.19
HATBH12/08	14.60	17.66	17.82	7.80	12.02	6.69	14.32	14.50	5.74	4.59	3.88
NSBH16/08	7.01	7.15	7.40	3.18	5.66	2.55	7.94	8.05	3.59	2.11	1.41
UABH10/08	3.27	4.13	4.24	1.98	2.59	2.05	3.96	4.17	1.86	1.99	1.59
DBH24/08	8.18	10.22	10.25	5.14	6.43	3.77	8.20	8.14	4.05	2.56	1.87
HB6/04	0.45	1.78	1.69	3.23	0.49	0.48	0.45	0.42	0.22	0.78	0.73
CT7/04	2.97	4.29	4.21	1.35	1.87	1.31	2.22	2.36	1.78	0.94	0.70
DI6/04	0.45	1.27	1.16	0.45	0.85	0.34	0.52	0.46	0.32	0.30	0.42
WI7/05	0.14	0.13	0.10	0.91	0.42	0.13	0.20	0.18	0.17	0.31	0.18
PPS5/05	2.23	1.55	1.66	0.36	3.25	1.65	2.74	2.45	0.21	0.43	0.27

^aErrors for AE6, SB1AE97, and LB1AE12, are reported on a per bond basis using eqs S1 and S2, so they are effectively mean unsigned errors in bond dissociation energies

III. FORTRAN routines for the MN12-L functional

MN12-L exchange:

```

Subroutine MN12Lx(F,D1F,RA,RB,D1RA,D1RB,TA,TB,NGrid)
*****
*
* MN12Lx evaluates the exchange part of MN12-L
* functional on the grid.
*
* OUTPUT:
*   F      - Functional values
*   D1F    - First derivatives with respect to RA, RB, GA, GB
*           TA, TB
*
* INPUT:
*   RA,B   - Spin densities
*   D1RA,B - Spin density gradients
*   TA,B   - Spin kinetic energy densities
*   NGrid  - number of grids
*
*****
      Implicit Real*8(A-H,O-Z)
C
      INTEGER NGrid
      REAL*8  F(NGrid),D1F(NGrid,7),RA(NGrid),RB(NGrid),

```

```
$          D1RA(NGrid,3),D1RB(NGrid,3),TA(NGrid),TB(NGrid)
Save One,Two,Three,Four,Five,Six,Seven,Eight,Nine
Data
One/1.0d0/,Two/2.0d0/,Three/3.0d0/,Four/4.0d0/,Five/5.0d0/,
$ Six/6.0d0/,Seven/7.0d0/,Eight/8.0d0/,Nine/9.0d0/
c
    dRA = 1
    dRB = 2
    dGA = 3
    dGB = 4
    dGC = 5
    dTA = 6
    dTB = 7
c
    G    = 0.004d+0
    ome = 2.5d+0
c
    CC000 = 6.73598D-01
    CC001 = -2.27060D+00
    CC002 = -2.61371D+00
    CC003 = 3.99361D+00
    CC004 = 4.63557D+00
    CC005 = 1.25068D+00
    CC010 = 8.44492D-01
    CC011 = -1.30117D+01
    CC012 = -1.77773D+01
    CC013 = -4.62721D+00
    CC014 = 5.97660D+00
    CC020 = 1.14290D+00
    CC021 = -2.04023D+01
    CC022 = -2.38284D+01
    CC023 = 7.11911D+00
    CC030 = -2.33573D+01
    CC031 = -1.62263D+01
    CC032 = 1.48273D+01
    CC100 = 1.44928D+00
    CC101 = 1.02060D+01
    CC102 = 4.40745D+00
    CC103 = -2.00819D+01
    CC104 = -1.25356D+01
    CC110 = -5.43503D+00
    CC111 = 1.65674D+01
    CC112 = 2.00023D+01
    CC113 = -2.51311D+00
    CC120 = 9.65844D+00
    CC121 = -3.82528D+00
    CC122 = -2.50000D+01
    CC200 = -2.07008D+00
```

```
CC201 = -9.95191D+00
CC202 = 8.73121D-01
CC203 = 2.21089D+01
CC210 = 8.82263D+00
CC211 = 2.49995D+01
CC212 = 2.50000D+01
CC300 = 6.85169D-01
CC301 = -7.40695D-02
CC302 = -6.78800D-01
```

c

```
Tiny = 1.0d-8
F12 = Two * Six
F24 = Four * Six
F28 = Four * Seven
F2o3 = Two / Three
F3o2 = Three / Two
Flo3 = One / Three
F4o3 = Four / Three
F7o3 = Seven / Three
F8o3 = Eight / Three
F10o3 = F2o3 * Five
F28o9 = F28 / Nine
PI = Four * ATan(One)
```

C

C

Local Spin Density factor.

C

```
Ax = -F3o2*(F4o3*PI)**(-Flo3)
```

c

c alpha component, beta component can be obtained
c by substituting RA, D1RA and TA with RB, D1RB and TB

c

```
Do 10 iG = 1, NGrid
  If(RA(i).gt.Tiny.and.TA(i).gt.Tiny) then
    F3o5 = Three/Five
    F6 = Six
    F5o3 = Five/Three
    pX = RA(i)
    GamX2 = D1RA(i)
    S2 = GamX2*pX**(-F8o3)
    U = G*S2/(One+G*S2)
    E = Ax*pX**F4o3
    Tau = TA(i)
    TauUEG = F3o5*((F6*PI*PI)**F2o3)*(pX**F5o3)
    Tsig = TauUEG/Tau
    Wsig = (Tsig - One)/(Tsig + One)
```

c

```
FU = U
FV = ome*pX**Flo3/(One+ome*pX**Flo3)
```



```

      FT = Wsig
c
      FMN12 = CC000 + FT*CC001 + FT**2*CC002 + FT**3*CC003 +
$      FT**4*CC004 + FT**5*CC005 +
$      FU*CC010 + FT*FU*CC011 + FT**2*FU*CC012 +
FT**3*FU*CC013 +
$      FT**4*FU*CC014 + FU**2*CC020 +
$      FT*FU**2*CC021 + FT**2*FU**2*CC022 + FT**3*FU**2*CC023
+
$      FU**3*CC030 + FT*FU**3*CC031 +
$      FT**2*FU**3*CC032 + FV*CC100 + FV*FT*CC101 +
$      FV*FT**2*CC102 + FV*FT**3*CC103 +
$      FV*FT**4*CC104 + FV*FU*CC110 + FV*FT*FU*CC111 +
$      FV*FT**2*FU*CC112 + FV*FT**3*FU*CC113 +
$      FV*FU**2*CC120 + FV*FT*FU**2*CC121 +
FV*FT**2*FU**2*CC122 +
$      FV**2*CC200 + FV**2*FT*CC201 +
$      FV**2*FT**2*CC202 + FV**2*FT**3*CC203 + FV**2*FU*CC210
+
$      FV**2*FT*FU*CC211 +
$      FV**2*FT**2*FU*CC212 + FV**3*CC300 + FV**3*FT*CC301 +
$      FV**3*FT**2*CC302
c
      F(i) = F(i) + E*FMN12
c
      If(MaxDrF.ge.1) then
        If(UseA) then
          ER = AR(i)
        else
          ER = F4o3*E/pX
        endIf
        S      = Sqrt(S2)
        GamX   = Sqrt(GamX2)
        SR     = -F4o3*S/pX
        SG     = S/GamX
        US     = Two*G*S/((One+G*S*S)**2)
c
        dFVdR = (ome/(Three*pX**F2o3))
$           *(One+ome*pX**F1o3)**(-Two)
c
        dWdT = Two/((One + Tsig)**2)
        dTdR = ((F6*PI*PI)**F2o3)*(pX**F2o3)/Tau
        dTdTau = -TauUEG/Tau**2
c
        dFTdR = dWdT*dTdR
        dFTdTau=dWdT*dTdTau
c
```

$$\begin{aligned} \text{dFMN12dFV} &= \text{CC100} + \text{FT*CC101} + \text{FT**2*CC102} + \\ &\text{FT**3*CC103} + \\ &\$ \quad \text{FT**4*CC104} + \text{FU*CC110} + \\ &\$ \quad \text{FT*FU*CC111} + \text{FT**2*FU*CC112} + \text{FT**3*FU*CC113} + \\ &\$ \quad \text{FU**2*CC120} + \text{FT*FU**2*CC121} + \\ &\$ \quad \text{FT**2*FU**2*CC122} + \text{Two*FV*CC200} + \text{Two*FV*FT*CC201} + \\ &\$ \quad \text{Two*FV*FT**2*CC202} + \text{Two*FV*FT**3*CC203} + \\ &\$ \quad \text{Two*FV*FU*CC210} + \\ &\text{Two*FV*FT*FU*CC211} + \text{Two*FV*FT**2*FU*CC212} + \\ &\$ \quad \text{Three*FV**2*CC300} + \text{Three*FV**2*FT*CC301} + \\ &\$ \quad \text{Three*FV**2*FT**2*CC302} \end{aligned}$$

c

$$\begin{aligned} \text{dFMN12dFU} &= \text{CC010} + \text{FT*CC011} + \text{FT**2*CC012} + \\ &\text{FT**3*CC013} + \\ &\$ \quad \text{FT**4*CC014} + \text{Two*FU*CC020} + \\ &\$ \quad \text{Two*FT*FU*CC021} + \text{Two*FT**2*FU*CC022} + \\ &\text{Two*FT**3*FU*CC023} + \\ &\$ \quad \text{Three*FU**2*CC030} + \text{Three*FT*FU**2*CC031} + \\ &\$ \quad \text{Three*FT**2*FU**2*CC032} + \text{FV*CC110} + \text{FV*FT*CC111} + \\ &\$ \quad \text{FV*FT**2*CC112} + \text{FV*FT**3*CC113} + \\ &\$ \quad \text{Two*FV*FU*CC120} + \\ &\text{Two*FV*FT*FU*CC121} + \text{Two*FV*FT**2*FU*CC122} + \\ &\$ \quad \text{FV**2*CC210} + \text{FV**2*FT*CC211} + \\ &\$ \quad \text{FV**2*FT**2*CC212} \end{aligned}$$

c

$$\begin{aligned} \text{dFMN12dFT} &= \text{CC001} + \text{Two*FT*CC002} + \text{Three*FT**2*CC003} + \\ &\$ \quad \text{Four*FT**3*CC004} + \text{Five*FT**4*CC005} + \text{FU*CC011} + \\ &\$ \quad \text{Two*FT*FU*CC012} + \\ &\text{Three*FT**2*FU*CC013} + \text{Four*FT**3*FU*CC014} + \\ &\$ \quad \text{FU**2*CC021} + \text{Two*FT*FU**2*CC022} + \\ &\$ \quad \text{Three*FT**2*FU**2*CC023} + \text{FU**3*CC031} + \\ &\text{Two*FT*FU**3*CC032} + \\ &\$ \quad \text{FV*CC101} + \text{Two*FV*FT*CC102} + \\ &\$ \quad \text{Three*FV*FT**2*CC103} + \text{Four*FV*FT**3*CC104} + \\ &\text{FV*FU*CC111} + \\ &\$ \quad \text{Two*FV*FT*FU*CC112} + \text{Three*FV*FT**2*FU*CC113} + \\ &\$ \quad \text{FV*FU**2*CC121} + \text{Two*FV*FT*FU**2*CC122} + \text{FV**2*CC201} + \\ &\$ \quad \text{Two*FV**2*FT*CC202} + \\ &\$ \quad \text{Three*FV**2*FT**2*CC203} + \text{FV**2*FU*CC211} + \\ &\$ \quad \text{Two*FV**2*FT*FU*CC212} + \text{FV**3*CC301} + \\ &\text{Two*FV**3*FT*CC302} \end{aligned}$$

c

$$\begin{aligned} \text{dFMN12dR} &= \\ \text{dFMN12dFV*dFVdR} &+ \text{dFMN12dFU*US*SR} + \text{dFMN12dFT*dFTdR} \\ \text{dFMN12dG} &= \text{dFMN12dFU*US*SG} \\ \text{dFMN12dT} &= \text{dFMN12dFT*dFTdTau} \end{aligned}$$

c

$$\text{D1F}(i, \text{dRA}) = \text{D1F}(i, \text{dRA}) + \text{ER*FMN12}$$

```

        $                + E*dFMN12dR
          D1F(i,dGA) = D1F(i,dGA) + E*dFMN12dG/(Two*GamX)
          D1F(i,dTA) = D1F(i,dTA) + E*dFMN12dT
        endIf
      endIf
10    Continue
      Return
    End
    
```

MN12-L correlation:

```

      Subroutine MN12Lc(F,D1F,RA,RB,D1RA,D1RB,TA,TB,NGrid)
      ****
      *
      * MN12Lc evaluates the correlation part of the MN11L
      * functionals on the grid.
      *
      * OUTPUT:
      *   F      - Functional values
      *   D1F    - First derivatives with respect to RA, RB, GA, GB
      *             TA, TB
      *
      * INPUT:
      *   RA,B   - Spin densities
      *   D1RA,B - Spin density gradients
      *   TA,B   - Spin kinetic energy densities
      *   NGrid  - number of grids
      *
      ****
      Real*8 LSDA
      INTEGER NGrid
      REAL*8  F(NGrid),D1F(NGrid,7),RA(NGrid),RB(NGrid),
      $      D1RA(NGrid,3),D1RB(NGrid,3),TA(NGrid),TB(NGrid)
      Integer dRA, dRB, dTA, dTB, dGA, dGB, dGC

      Save Zero, F1, F2, F3, F4, F5, F6, F7, F8, F9, F10, F11
      Data Zero/0.0d0/, F1/1.0d0/, F2/2.0d0/, F3/3.0d0/,
      $  F4/4.0d0/, F5/5.0d0/, F6/6.0d0/,
      F7/7.0d0/,F8/8.0d0/,F9/9.0d0/,
      $  F10/10.0d0/, F11/11.0d0/
      parameter( pi = 3.1415926535897932384626433832795d0 )

      dRA = 1
      dRB = 2
      dGA = 3
      dGB = 4
      dGc = 5
      dTA = 6
    
```

dTB = 7

F4o3 = F4 / F3

F1o3 = F1 / F3

F5o3 = F5 / F3

F2o3 = F2 / F3

Tiny = 1.0d-8

Pi34 = F3/(F4*Pi)

at00= 8.84461D-01

at01= -2.20228D-01

at02= 5.70137D+00

at03= -2.56238D+00

at04= -9.64683D-01

at05= 1.98218D-01

at06= 1.01998D+01

at07= 9.78935D-01

at08= -1.51272D+00

at09= 0.00000D+00

at10= 0.00000D+00

at11= 0.00000D+00

bt00= 5.32395D-01

bt01= -5.83191D+00

bt02= 3.88239D+00

bt03= 5.87849D+00

bt04= 1.49323D+01

bt05= -1.37464D+01

bt06= -8.49233D+00

bt07= -2.48655D+00

bt08= -1.82235D+01

bt09= 0.00000D+00

bt10= 0.00000D+00

bt11= 0.00000D+00

DO i = 1,NGrid

RhoA = RA(i)

RhoB = RB(i)

Rho = RhoA + RhoB

TauA = TA(i)/F2

TauB = TB(i)/F2

Tau = TauA + TauB

If(Rho.gt.Tiny.and.Tau.gt.Tiny) then

RS = (Pi34/Rho) ** F1o3

Zeta = (RhoA-RhoB)/Rho

TauUEG=F3*(F3*Pi*Pi)**(F2o3)*Rho**(F5o3)/F10

Tsig =TauUEG/Tau

```
Wsig =(Tsig - F1)/(Tsig + F1)
Fsig1=(at00 + Wsig*(at01 + Wsig*(at02 + Wsig*(at03 +
Wsig*(
&          at04 + Wsig*(at05 + Wsig*(at06 + Wsig*(at07 +
Wsig*(
&          at08 + Wsig*(at09 +
Wsig*(at10+Wsig*at11))))))))))

Fsig2=(bt00 + Wsig*(bt01 + Wsig*(bt02 + Wsig*(bt03 +
Wsig*(
&          bt04 + Wsig*(bt05 + Wsig*(bt06 + Wsig*(bt07 +
Wsig*(
&          bt08 + Wsig*(bt09 +
Wsig*(bt10+Wsig*bt11))))))))))

Y = (D1RA(i,1) + D1RB(i,1))**2
$   + (D1RA(i,2) + D1RB(i,2))**2
$   + (D1RA(i,3) + D1RB(i,3))**2
GRho = Sqrt(Y)
c
c   lsdac is a subroutine to evaluate the Perdew-Wang-91
correlation functional
c   local spin density approximation (LSDA) to the
correlation energy of a uniform
c   electron gas. (Phys. Rev. B 45, 13244 (1992)). Users
should provid their own
c   for this LSDA correlation functional or they may find
this routine on Kieron
c   Burke's Web site at http://dft.uci.edu/pubs/PBE.asc
c

Call lsdac(RS,Zeta,PotLC,dLdS,dLdZ)
LSDA = Rho*PotLC
c
c   PBEH0 is a subroutine to evaluate the H0 term in the PBE
correlation functional
c   (Phys. Rev. Lett. 77, 3865 - 3868 (1996)) Users should
provid their own
c   for this H0 subroutine or they may find this routine on
Kieron
c   Burke's Web site at http://dft.uci.edu/pubs/PBE.asc
c

Call
PBEH0(Rho,GRho,RS,Zeta,PotLC,dLdS,dLdZ,H,dHdR,dHdG,dHdZ)
GGA = Rho*H
E1 = LSDA*Fsig1
E2 = GGA*Fsig2
F(i) = F(i)+ E1 +E2
```

```

c
c      functional derivatives
c
      RSP = -RS/(F3*Rho)
      dZdA = (F1-Zeta)/Rho
      dZdB = (-F1-Zeta)/Rho
      dLdRA = dLdS*RSP + dLdZ*dZdA
      dLdRB = dLdS*RSP + dLdZ*dZdB
      dF1dW=( at01 + Wsig*(F2  *at02 + Wsig*(F3*at03 + Wsig*(
&
      F4  *at04 + Wsig*(F5  *at05 + Wsig*(F6  *at06 +
Wsig*(
&
      F7*at07 + Wsig*(F8*at08 + Wsig*(F9  *at09 +
Wsig*(
&
      F10  *at10+ Wsig*F11*at11))))))))))
      dF2dW=( bt01 + Wsig*(F2  *bt02 + Wsig*(F3*bt03 + Wsig*(
&
      F4  *bt04 + Wsig*(F5  *bt05 + Wsig*(F6  *bt06 +
Wsig*(
&
      F7*bt07 + Wsig*(F8*bt08 + Wsig*(F9  *bt09 +
Wsig*(
&
      F10  *bt10+ Wsig*F11*bt11))))))))))
      dWdT = F2/((F1 + Tsig)**2)
      dTdR = Tsig*F5/(F3*Rho)
      dTdTau = -Tsig/Tau
      dF1dR = dF1dW*dWdT*dTdR
      dF1dTau=dF1dW*dWdT*dTdTau
      dF2dR = dF2dW*dWdT*dTdR
      dF2dTau=dF2dW*dWdT*dTdTau
      dLDdRA = PotLC + Rho*dLdRA
      dLDdRB = PotLC + Rho*dLdRB
      dHdRA = dHdR + dHdZ*dZdA
      dHdRB = dHdR + dHdZ*dZdB
      dGRhody = F1/(F2*GRho)
      dHdY = dHdG * dGRhody
      dHdGA = dHdY
      dHdGB = dHdY
      dHdGC = dHdY*F2
      dGGAdRA = H + Rho*dHdRA
      dGGAdRB = H + Rho*dHdRB
      dGGAdGA = Rho*dHdGA
      dGGAdGB = dGGAdGA
      dGGAdGC = Rho*dHdGC
c
      dE1dRA = dLDdRA*Fsig1 + LSDA*dF1dR
      dE1dRB = dLDdRB*Fsig1 + LSDA*dF1dR
      dE1dKA = LSDA*dF1dTau
      dE1dKB = dE1dKA
c
    
```

```
dE2dRA = dGGAdRA*Fsig2 + GGA*dF2dR
dE2dRB = dGGAdRB*Fsig2 + GGA*dF2dR
dE2dKA = GGA*dF2dTau
dE2dKB = dE2dKA
dE2dGA = dGGAdGA*Fsig2
dE2dGB = dGGAdGB*Fsig2
dE2dGC = dGGAdGC*Fsig2

D1F(i,dRA)=D1F(i,dRA) + dE1dRA + dE2dRA
D1F(i,dRB)=D1F(i,dRB) + dE1dRB + dE2dRB
D1F(i,dTA)=D1F(i,dTA) + (dE1dKA + dE2dKA)/F2
D1F(i,dTB)=D1F(i,dTB) + (dE1dKB + dE2dKA)/F2
D1F(i,dGA)=D1F(i,dGA) + dE2dGA
D1F(i,dGB)=D1F(i,dGB) + dE2dGB
C GC is the dot product of the vectors D1RA and D1RB
D1F(i,dGC)=D1F(i,dGC) + dE2dGC
Endif
Enddo
Return
End
```

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