Supporting Information for:


Roberto Peverati and Donald G. Truhlar*

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 (IP13/03$^{1-4}$) contains data from six atoms: C, S, O, P, Si and Cl, and seven molecules (SH, Cl$_2$, OH, O$_2$, PH, PH$_2$ and S$_2$). 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, $R_e = 1.596$ Å). 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 set$^{4}$ 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+2fg$^6$ basis for Fe and the def2-QZVPP basis$^7$ 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,\textsuperscript{8,10} while they are included in the calculations of FeC within the SDD relativistic effective core potential.\textsuperscript{6} The reference data for the IP21 database are collected in Table S1.

\textit{Table S1.} Reference data (kcal/mol) for the IP21 database.

<table>
<thead>
<tr>
<th>IP13/03</th>
<th>Reference</th>
<th>IPM8</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>259.7</td>
<td>Cr</td>
<td>156.01</td>
</tr>
<tr>
<td>S</td>
<td>238.9</td>
<td>Cu</td>
<td>178.17</td>
</tr>
<tr>
<td>SH</td>
<td>238.9</td>
<td>FeC</td>
<td>173.71</td>
</tr>
<tr>
<td>Cl</td>
<td>299.1</td>
<td>Mo</td>
<td>163.71</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>265.3</td>
<td>Pd</td>
<td>192.24</td>
</tr>
<tr>
<td>OH</td>
<td>299.1</td>
<td>Rh</td>
<td>172.11</td>
</tr>
<tr>
<td>O</td>
<td>313.9</td>
<td>Ru</td>
<td>169.86</td>
</tr>
<tr>
<td>O(_2)</td>
<td>278.9</td>
<td>Zn</td>
<td>216.63</td>
</tr>
<tr>
<td>P</td>
<td>241.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PH</td>
<td>234.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PH(_2)</td>
<td>226.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(_2)</td>
<td>216.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>187.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) \textbf{AE17.} The MG3S basis set that we previously used for the atomic energies database (AE17\textsuperscript{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 set\textsuperscript{13} for H, He, and atoms from Be to Ne and from Al to Ar, while we used the cc-pCVQZ basis set\textsuperscript{14} for Li, Be, Na and Mg atoms.

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

- MGAE109/11:\textsuperscript{1,15} 109 main group atomization energies, for which we used the MG3S basis set.\textsuperscript{4}
- SRMBE12:\textsuperscript{16} 12 single-reference metal bond energies, for which we used the def2-TZVP basis set.\textsuperscript{17,18}
- MRBE10:\textsuperscript{16} 10 multi-reference bond energies, for which we used the def2-TZVP basis set.\textsuperscript{17,18}
- IsoL6:\textsuperscript{19} 6 isomerization energies of large organic molecules, for which we used the MG3SXP basis set.\textsuperscript{20}
• EA13/03: 13 electron affinities, for which we used the MG3S basis set.
• PA8: 8 proton affinities, for which we used the MG3S basis set.
• ABDE4/05 and ABDEL8: 4 and 8 alkyl bond dissociation reaction energies, for which we used the MG3S basis set.
• HC7/11: 7 hydrocarbons, for which we used the 6-311+G(2df,2p) basis set.
• πTC13: 13 π system thermochemistry, for which we used the MG3S basis set.
• HTBH38/08: 38 hydrogen-transfer and 38 non-hydrogen-transfer barrier heights, for which we used the MG3S basis set.
• NCCE31/05: 31 noncovalent complexation energies, for which we used the MG3S basis set.
• DC9/12: 9 difficult cases, for which we used the MG3S basis set.
• SSLC34: 34 semiconductors lattice constants, for which we used the m-6-311G* basis set.
• DG6: 6 geometries of diatomic molecules, for which we used the 6-311+G(2df,2p) basis set.
• SL34: 34 semiconductors lattice constants, for which we used the m-6-311G* basis set.
• SBG31: 31 semiconductors band gaps, for which we used the m-6-311G* basis set.
• SSCE8: 8 solid-state cohesive energies, for which we used the m-6-311G* basis set.
• MGBL20: 20 main group bond length, for which we used the 6-311+G(2df,2p) basis set.

(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: 6 atomization energies (from MGAE109/11).
SB1AE97: small-B1 atomization energies (from MGAE109/11).
LB1AE12: large-B1 atomization energies (from MGAE109/11).
TMBE15: 15 transition metals bond energies (from SRMBE13 and MRBE10).
MBE18: 18 metals bond energies (from SRMBE13 and MRBE10).
IP13/03: 13 ionization potentials of main group atoms and molecules (from IP21).
IPM8: 8 ionization potentials of metal atoms and metal containing molecule (from IP21).
πE3/06: three π systems isomerization energies (from πTC13).
PA-CP5/06: five proton affinities of conjugated polyenes (from πTC13).
PA-SB5/06: five proton affinities of Schiff basis (from πTC13).
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:

\[
\text{MUE}_{PB} = \frac{1}{n_{\text{bond}}} \frac{1}{n_{\text{molec}}} \sum_{i=1}^{n_{\text{molec}}} \frac{|A E_i - A E_i^{\text{Ref}}|}{n_{\text{molec}}}
\]

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

\[
\begin{align*}
    n_{\text{bond}} &= 4.71 \text{ for MGAE109/11}, \\
    n_{\text{bond}} &= 5.10 \text{ for SB1AE97}, \\
    n_{\text{bond}} &= 1.33 \text{ for LB1AE12}, \\
    n_{\text{bond}} &= 4.67 \text{ for AE6}, \\
    n_{\text{bond}} &= 9.22 \text{ for DC9/12}.
\end{align*}
\]

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

\[
\text{MUE(BC345)} = \frac{1}{n_{\text{tot}}} \{ 109 \times \text{MUE}_{PB}(\text{MGAE109/11}) + 13 \times \text{MUE}(\text{SRMBE13}) + 10 \times \text{MUE}(\text{MRBE10}) + 6 \times \text{MUE}(\text{IsoL6/11}) + 21 \times \text{MUE}(\text{IP21}) + 13 \times \text{MUE}(\text{EA13/03}) + 8 \times \text{MUE}(\text{PA8/06}) + \}
\]
where $n_{\text{tot}}$ 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.

| Subset            | MUE   | MSE   | Largest $|\varepsilon|$ | Smallest $|\varepsilon|$ |
|-------------------|-------|-------|-----------|----------------|----------------|
| 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            |
| $\pi$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

<table>
<thead>
<tr>
<th>Subset</th>
<th>AE6$^a$</th>
<th>SB1AE97$^a$</th>
<th>LB1AE12$^a$</th>
<th>TMBE15</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>3.16</td>
<td>2.77</td>
<td>12.98</td>
<td>9.62</td>
</tr>
<tr>
<td>SOGGA</td>
<td>7.53</td>
<td>7.36</td>
<td>23.27</td>
<td>14.96</td>
</tr>
<tr>
<td>PBEsol</td>
<td>7.45</td>
<td>7.51</td>
<td>22.67</td>
<td>14.53</td>
</tr>
<tr>
<td>SOGGA11</td>
<td>1.78</td>
<td>1.47</td>
<td>8.38</td>
<td>11.67</td>
</tr>
<tr>
<td>N12</td>
<td>0.91</td>
<td>1.12</td>
<td>6.03</td>
<td>5.47</td>
</tr>
<tr>
<td>HSE</td>
<td>0.94</td>
<td>0.82</td>
<td>2.81</td>
<td>14.99</td>
</tr>
<tr>
<td>TPSS</td>
<td>1.02</td>
<td>0.99</td>
<td>3.70</td>
<td>7.58</td>
</tr>
<tr>
<td>revTPSS</td>
<td>1.17</td>
<td>0.85</td>
<td>4.13</td>
<td>7.08</td>
</tr>
<tr>
<td>M06-L</td>
<td>0.64</td>
<td>0.83</td>
<td>2.25</td>
<td>4.43</td>
</tr>
<tr>
<td>M11-L</td>
<td>1.00</td>
<td>0.68</td>
<td>2.94</td>
<td>7.74</td>
</tr>
<tr>
<td>MN12-L</td>
<td>0.65</td>
<td>0.63</td>
<td>2.72</td>
<td>5.26</td>
</tr>
</tbody>
</table>
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),

---

Errors 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.
$\quad D1RA(NGrid,3), D1RB(NGrid,3), TA(NGrid), TB(NGrid)$

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/

$\quad dRA = 1$
$\quad dRB = 2$
$\quad dGA = 3$
$\quad dGB = 4$
$\quad dGC = 5$
$\quad dTA = 6$
$\quad dTB = 7$

$\quad G = 0.004d+0$
$\quad ome = 2.5d+0$

$\quad CC000 = 6.73598D-01$
$\quad CC001 = -2.27060D+00$
$\quad CC002 = -2.61371D+00$
$\quad CC003 = 3.99361D+00$
$\quad CC004 = 4.63557D+00$
$\quad CC005 = 1.25068D+00$
$\quad CC010 = 8.44492D-01$
$\quad CC011 = -1.30117D+01$
$\quad CC012 = -1.77773D+01$
$\quad CC013 = -4.62721D+00$
$\quad CC014 = 5.97660D+00$
$\quad CC020 = 1.14290D+00$
$\quad CC021 = -2.04023D+01$
$\quad CC022 = -2.38284D+01$
$\quad CC023 = 7.11911D+00$
$\quad CC030 = -2.33573D+01$
$\quad CC031 = -1.62263D+01$
$\quad CC032 = 1.48273D+01$
$\quad CC100 = 1.44928D+00$
$\quad CC101 = 1.02060D+01$
$\quad CC102 = 4.40745D+00$
$\quad CC103 = -2.00819D+01$
$\quad CC104 = -1.25356D+01$
$\quad CC110 = -5.43503D+00$
$\quad CC111 = 1.65674D+01$
$\quad CC112 = 2.00023D+01$
$\quad CC113 = -2.51311D+00$
$\quad CC120 = 9.65844D+00$
$\quad CC121 = -3.82528D+00$
$\quad CC122 = -2.50000D+01$
$\quad CC200 = -2.07008D+00$
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  

Tiny = 1.0d-8  
F12   = Two * Six  
F24   = Four * Six  
F28   = Four * Seven  
F2o3  = Two / Three  
F3o2  = Three / Two  
F1o3  = One / Three  
F4o3  = Four / Three  
F7o3  = Seven / Three  
F8o3  = Eight / Three  
F10o3 = F2o3 * Five  
F28o9 = F28 / Nine  
PI    = Four * ATan(One)  

Local Spin Density factor.

Ax = -F3o2*(F4o3*PI)**(-F1o3)  
alpha component, beta component can be obtained  
by substituting RA, D1RA and TA with RB, D1RB and TB  

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)  

FU = U  
FV = ome*pX**F1o3/(One+ome*pX**F1o3)
FT = Wsig

\[
\begin{align*}
FT &= F(i) + E*FMN12 \\
F(i) &= F(i) + E*FMN12 \\
\text{If}(\text{MaxDrF} \geq 1) \text{ then} & \\
\text{If}(\text{UseA}) \text{ then} & \\
ER &= AR(i) & \\
\text{else} & \\
ER &= F4o3*E/pX \\
\text{endIf} & \\
S &= \sqrt{S2} \\
GamX &= \sqrt{GamX2} \\
SR &= -F4o3*S/pX \\
SG &= S/GamX \\
US &= Two*G*S/((One+G*S*S)**2) \\
\]
\[
dFMN12dFV = CC100 + FT*CC101 + FT**2*CC102 + \\
FT**3*CC103 + \\
\$ FT**4*CC104 + FU*CC110 + \\
\$ FT*FU*CC111 + FT**2*FU*CC112 + FT**3*FU*CC113 + \\
\$ FU**2*CC120 + FT*FU**2*CC121 + \\
\$ FT**2*FU**2*CC122 + Two*FV*CC200 + Two*FV*FT*CC201 + \\
\$ Two*FV*FT**2*CC202 + Two*FV*FT**3*CC203 + \\
\$ Two*FV*FU*CC210 + \\
\$ Three*FV**2*CC300 + Three*FV**2*FT*CC301 + \\
\$ Three*FV**2*FT**2*CC302 \\
c
\[
dFMN12dFU = CC010 + FT*CC011 + FT**2*CC012 + \\
FT**3*CC013 + \\
\$ FT**4*CC014 + Two*FU*CC020 + \\
\$ Two*FT*FU*CC021 + Two*FT**2*FU*CC022 + \\
Two*FT**3*FU*CC023 + \\
\$ Three*FU**2*CC030 + Three*FT*FU**2*CC031 + \\
\$ Three*FT**2*FU**2*CC032 + FV*CC110 + FV*FT*CC111 + \\
\$ FV*FT**2*CC112 + FV*FT**3*CC113 + \\
\$ Two*FV*FU*CC120 + \\
Two*FV*FT*FU*CC121+Two*FV*FT**2*FU*CC122+ \\
\$ FV**2*CC210 + FV**2*FT*CC211 + \\
\$ FV**2*FT**2*CC212 \\
c
\[
dFMN12dFT = CC001 + Two*FT*CC002 + Three*FT**2*CC003 + \\
\$ Four*FT**3*CC004 + Five*FT**4*CC005 + FU*CC011 + \\
\$ Two*FT*FU*CC012 + \\
Three*FT**2*FU*CC013+Four*FT**3*FU*CC014+ \\
\$ FU**2*CC021 + Two*FT*FU**2*CC022 + \\
\$ Three*FT**2*FU**2*CC023 + FU**3*CC031 + \\
Two*FT*FU**3*CC032 + \\
\$ FV*CC101 + Two*FV*FT*CC102 + \\
\$ Three*FV*FT**2*CC103 + Four*FV*FT**3*CC104 + \\
FV*FU*CC111 + \\
\$ Two*FV*FT*FU*CC112 + Three*FV*FT**2*FU*CC113 + \\
\$ FV*FU**2*CC121 + Two*FV*FT*FU**2*CC122 + FV**2*CC201 + \\
\$ Two*FV**2*FT*CC202 + \\
\$ Three*FV**2*FT**2*CC203 + FV**2*FU*CC211 + \\
\$ Two*FV**2*FT*FU*CC212 + FV**3*CC301 + \\
Two*FV**3*FT*CC302 \\
c
\[
dFMN12dR = 
dFMN12dFV*dFVdR+dFMN12dFU*US*SR+dFMN12dFT*dFTdR 
dFMN12dG = dFMN12dFU*US*SG 
dFMN12dT = dFMN12dFT*dFTdTau 
c
D1F(i,dRA) = D1F(i,dRA) + 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

\[ F4o3 = \frac{F4}{F3} \]
\[ F1o3 = \frac{F1}{F3} \]
\[ F5o3 = \frac{F5}{F3} \]
\[ F2o3 = \frac{F2}{F3} \]

Tiny = 1.0d-8

\[ Pi34 = \frac{F3}{(F4*\pi)} \]

\[ at00 = 8.84461D-01 \]
\[ at01 = -2.20228D-01 \]
\[ at02 = 5.70137D+00 \]
\[ at03 = -2.56238D+00 \]
\[ at04 = -9.64683D-01 \]
\[ at05 = 1.98218D-01 \]
\[ at06 = 1.01998D+01 \]
\[ at07 = 9.78935D-01 \]
\[ at08 = -1.51272D+00 \]
\[ at09 = 0.00000D+00 \]
\[ at10 = 0.00000D+00 \]
\[ at11 = 0.00000D+00 \]

\[ bt00 = 5.32395D-01 \]
\[ bt01 = -5.83191D+00 \]
\[ bt02 = 3.88239D+00 \]
\[ bt03 = 5.87849D+00 \]
\[ bt04 = 1.49323D+01 \]
\[ bt05 = -1.37464D+01 \]
\[ bt06 = -8.49233D+00 \]
\[ bt07 = -2.48655D+00 \]
\[ bt08 = -1.82235D+01 \]
\[ bt09 = 0.00000D+00 \]
\[ bt10 = 0.00000D+00 \]
\[ bt11 = 0.00000D+00 \]

DO i = 1,NGrid
\[ \text{RhoA} = RA(i) \]
\[ \text{RhoB} = RB(i) \]
\[ \text{Rho} = \text{RhoA} + \text{RhoB} \]
\[ \text{TauA} = TA(i)/F2 \]
\[ \text{TauB} = TB(i)/F2 \]
\[ \text{Tau} = \text{TauA} + \text{TauB} \]

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

\[ RS = (Pi34/Rho)^{F1o3}\]
\[ \text{Zeta} = (\text{RhoA}-\text{RhoB})/\text{Rho} \]
\[ \text{TauUEG} = F3*(F3*Pi*Pi)**(F2o3)*\text{Rho}**(F5o3)/F10 \]
\[ \text{Tsig} = \text{TauUEG}/\text{Tau} \]
Wsig = (Tsig - F1)/(Tsig + F1)
Fsig1 = (at00 + Wsig*(at01 + Wsig*(at02 + Wsig*(at03 +
   & 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)

lsdac is a subroutine to evaluate the Perdew-Wang-91
correlation functional
clocal spin density approximation (LSDA) to the
correlation energy of a uniform
should provid their own
cfor this LSDA correlation functional or they may find
this routine on Kieron
c
Call lsdac(RS,Zeta,PotLC,dLdS,dLdZ)
LSDA = Rho*PotLC
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
cfor this H0 subroutine or they may find this routine on
Kieron
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
functional derivatives

\[
\begin{align*}
RSP &= -RS/(F3*\text{Rho}) \\
dZdA &= (F1-Zeta)/\text{Rho} \\
dZdB &= (-F1-Zeta)/\text{Rho} \\
dLdRA &= dLdS*RSP + dLdZ*dZdA \\
dLdRB &= dLdS*RSP + dLdZ*dZdB \\
dF1dW &= (at01 + Wsig*(F2 *at02 + Wsig*(F3*at03 + Wsig*(F4 *at04 + Wsig*(F5 *at05 + Wsig*(F6 *at06 + Wsig*(F7*at07 + Wsig*(F8*at08 + Wsig*(F9 *at09 + Wsig*(F10 *at10+ Wsig*F11*at11)))))))))) \\
dF2dW &= (bt01 + Wsig*(F2 *bt02 + Wsig*(F3*bt03 + Wsig*(F4 *bt04 + Wsig*(F5 *bt05 + Wsig*(F6 *bt06 + Wsig*(F7*bt07 + Wsig*(F8*bt08 + Wsig*(F9 *bt09 + Wsig*(F10 *bt10+ Wsig*F11*bt11)))))))))) \\
dWdT &= F2/((F1 + Tsig)**2) \\
dTdR &= Tsig*F5/(F3*\text{Rho}) \\
dTdTau &= -Tsig/Tau \\
dF1dR &= dF1dW*dWdT*dTdR \\
dF1dTau=dF1dW*dWdT*dTdTau \\
dF2dR &= dF2dW*dWdT*dTdR \\
dF2dTau=dF2dW*dWdT*dTdTau \\
dLdRA &= \text{PotLC} + \text{Rho}*dLdRA \\
dLdRB &= \text{PotLC} + \text{Rho}*dLdRB \\
dHdRA &= dHdR + dHdZ*dZdA \\
dHdRB &= dHdR + dHdZ*dZdB \\
dGRhodY &= F1/(F2*GRho) \\
dHdY &= dHdG * dGRhodY \\
dHdGA &= dHdY \\
dHdGB &= dHdY \\
dHdGC &= dHdY*F2 \\
dGGAdRA &= H + \text{Rho}*dHdRA \\
dGGAdRB &= H + \text{Rho}*dHdRB \\
dGGAdGA &= \text{Rho}*dHdGA \\
dGGAdGB &= dGGAdGA \\
dGGAdGC &= \text{Rho}*dHdGC \\
de1dRA &= dLdDRA*Fsig1 + LSDA*dF1dR \\
de1dRB &= dLdDRA*Fsig1 + LSDA*dF1dR \\
de1dKA &= LSDA*dF1dTau \\
de1dKB &= e1dKA
\end{align*}
\]
\[ \begin{align*} 
\text{dE}2\text{dRA} &= \text{dGGAdRA} \cdot \text{Fsig2} + \text{GGA} \cdot \text{dF}2\text{dR} \\
\text{dE}2\text{dRB} &= \text{dGGAdRB} \cdot \text{Fsig2} + \text{GGA} \cdot \text{dF}2\text{dR} \\
\text{dE}2\text{dKA} &= \text{GGA} \cdot \text{dF}2\text{dTau} \\
\text{dE}2\text{dKB} &= \text{dE}2\text{dKA} \\
\text{dE}2\text{dGA} &= \text{dGGAdGA} \cdot \text{Fsig2} \\
\text{dE}2\text{dGB} &= \text{dGGAdGB} \cdot \text{Fsig2} \\
\text{dE}2\text{dGC} &= \text{dGGAdGC} \cdot \text{Fsig2} \\
\text{D1F}(i, \text{dRA}) &= \text{D1F}(i, \text{dRA}) + \text{dE}1\text{dRA} + \text{dE}2\text{dRA} \\
\text{D1F}(i, \text{dRB}) &= \text{D1F}(i, \text{dRB}) + \text{dE}1\text{dRB} + \text{dE}2\text{dRB} \\
\text{D1F}(i, \text{dTA}) &= \text{D1F}(i, \text{dTA}) + \frac{(\text{dE}1\text{dKA} + \text{dE}2\text{dKA})}{\text{F}2} \\
\text{D1F}(i, \text{dTB}) &= \text{D1F}(i, \text{dTB}) + \frac{(\text{dE}1\text{dKB} + \text{dE}2\text{dKA})}{\text{F}2} \\
\text{D1F}(i, \text{dGA}) &= \text{D1F}(i, \text{dGA}) + \text{dE}2\text{dGA} \\
\text{D1F}(i, \text{dGB}) &= \text{D1F}(i, \text{dGB}) + \text{dE}2\text{dGB} \\
\text{C} \quad \text{GC} \text{ is the dot product of the vectors D1RA and D1RB} \\
\text{D1F}(i, \text{dGC}) &= \text{D1F}(i, \text{dGC}) + \text{dE}2\text{dGC} \\
\end{align*} \]

End if
End do
Return
End

References:

4611–4620.