Supporting Information:
Explicitly correlated double hybrid DFT: a comprehensive analysis of the basis set convergence on the GMTKN55 database

Nisha Mehta and Jan M. L. Martin*

Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel

E-mail: gershom@weizmann.ac.il
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**SI.1  How to run DHDF-F12 calculations**

**SI.1.1  Sample input for B2GP-PLYP-F12:**

```molpro
SI.1.1.1 Sample input for B2GP-PLYP-F12:

```
gthresh,energy=1d-9, throvl=1d-9
ANGSTROM
geomtyp=xyz
geom=
include struc.xyz
! end geometry
thecharge=0
multiplicity=1
```

```molpro
basis,avdz-f12
{DF=KS,b,lyp;dh,0.65,0.36;wf,spin=$multiplicity-1,CHARGE=$thecharge;}
eksf12=ENERGY;
DF=mp2-f12, GEM_BETA=0.9
! For close shell systems
if($multiplicity.eq.1)then
eglptf12=(ENERGY-ENERGGR)*0.36
ecabs=EF12_SINGLES
else
! For close shell systems
eglptf12=(ENERG_VV+ENERG_CC+ENERG_CV)*0.36
ecabs=EF12_SINGLES
endif
ETOT=eksf12+eglptf12+ecabs
show,*
!Note that the DFT-D3(BJ) correction is not included in this molpro input.
```

**SI.1.2  Sample input for revDSD-PBEP86-F12:**

```molpro
SI.1.2 Sample input for revDSD-PBEP86-F12:

```
gthresh,energy=1d-9
ANGSTROM
geomtyp=xyz
geom=
include struc.xyz
! end geometry
thecharge=0
multiplicity=1
```

```molpro
cDFTc=0.4210
cXHF=0.69
c2ab=0.5922
c2ss=0.0636
basis,vdz-f12
{DF=ks,pbex,p86;dh,cXHF,1.00-cDFTc; wf,spin=$multiplicity-1,CHARGE=$thecharge;}
EKS=ENERGY;
DF=mp2-f12,scsfacs=c2ab/(1.00-cDFTc),scsfact=c2ss/(1.00-cDFTc), GEM_BETA=0.9
SCSMP2=(EMP2_SING+EMP2_TRIP/3)*1.02280+EMP2_TRIP*2/3*0.10984
SCSF12=(EF12_SING+EF12_TRIP/3)*1.02280+EF12_TRIP*2/3*0.10984
ECABS=EF12_SINGLES
ETOT=EKS+ECABS+(SCSMP2+SCSF12)*0.5790
show,*
!This is the end of Molpro input
!Note that the DFT-D4 dispersion correction is not included in this molpro input.
```
**SI.2 Analysis of weighted total mean signed deviation (WTMSD2)**

Table S1: WTMSD2 values (kcal/mol) of conventional and explicitly correlated B2GP-PLYP-D3(BJ) for GMTKN55 and its categories relative to Ref. S1 reference data. A positive sign indicates overestimation.

|          | B2GP-PLYP-D3(BJ) | B2GP-PLYP-F12-D3(BJ) |
|----------|------------------|----------------------|
|          | WTMSD2 | THERMO | BARRIERS | LARGE | CONF | INTERMOL | WTMSD2 | THERMO | BARRIERS | LARGE | CONF | INTERMOL |
| VDZ      | 2.738  | -0.862 | -0.536  | -0.331 | 2.343 | 2.124    | VDZ-F12 | 0.717  | 0.145   | -0.127 | -0.009 | 0.269  | 0.468   |
| VDZ*     | 3.451  | -0.134 | -0.396  | -0.331 | 2.343 | 1.970    | VDZ-F12 | 0.741  | 0.141   | -0.125 | -0.003 | 0.268  | 0.459   |
| VTZ      | 1.083  | -0.134 | -0.396  | -0.319 | 0.527 | 1.405    | VTZ-F12 | 0.753  | 0.155   | -0.127 | -0.003 | 0.268  | 0.469   |
| VTZ*     | 1.382  | -0.279 | -0.289  | -0.400 | 0.864 | 1.126    | VTZ-F12 | 0.714  | 0.168   | -0.128 | 0.006  | 0.279  | 0.459   |
| VTZ**    | 1.759  | 0.114  | -0.195  | -0.400 | 0.864 | 1.015    | VTZ-F12*| 0.755  | 0.177   | -0.129 | 0.006  | 0.279  | 0.422   |
| VQZ      | 0.703  | -0.084 | -0.223  | 0.010  | 0.448 | 0.774    | V[D,T]Z-F12 | 0.748  | 0.177   | -0.133 | 0.008  | 0.283  | 0.413   |
| VQZ*     | 0.703  | 0.107  | -0.146  | 0.009  | 0.269 | 0.570    | VQZ-F12*| 0.689  | 0.180   | -0.120 | 0.005  | 0.269  | 0.364   |
| V[Q,T]Z  | 1.158  | 0.067  | -0.242  | 0.031  | 0.367 | 0.994    | V[Q,T]Z-F12 | 0.683  | 0.177   | -0.123 | 0.004  | 0.259  | 0.365   |
| V[Q,T]Z* | 1.340  | 0.181  | -0.145  | 0.031  | 0.367 | 0.995    | V[Q,T]Z-F12*| 0.685  | 0.181   | -0.119 | 0.004  | 0.259  | 0.360   |
| V[Q,T]Z**| 1.037  | 0.181  | -0.145  | 0.032  | 0.270 | 0.700    |                     |                  |        |        |        |        |        |
| V5Z      | 0.745  | 0.154  | -0.123  | 0.066  | 0.298 | 0.418    |                     |                  |        |        |        |        |        |
| V5Z*     | 0.745  | 0.154  | -0.123  | 0.066  | 0.298 | 0.418    |                     |                  |        |        |        |        |        |
| V5Z**    | 0.745  | 0.154  | -0.123  | 0.066  | 0.298 | 0.418    |                     |                  |        |        |        |        |        |
| def2-TZVPP | 0.692  | -0.184 | -0.292  | -0.004 | 0.512 | 0.560    |                     |                  |        |        |        |        |        |
| def2-TZVPP* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPP** | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD | 0.844  | -0.040 | -0.130  | 0.044  | 0.274 | 0.696    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD** | 0.692  | -0.184 | -0.292  | -0.004 | 0.512 | 0.560    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD** | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD** | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD** | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD** | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
| def2-TZVPPFD* | 0.731  | -0.084 | -0.127  | -0.004 | 0.512 | 0.604    |                     |                  |        |        |        |        |        |
Table S2: WTMSD2 values (kcal/mol) of conventional and explicitly correlated B2GP-PLYP-D3(BJ) for GMTKN55 and its categories relative to the B2GP-PLYP-F12-D3(BJ)/V\{T,Q\}Z-F12* reference data. A positive sign indicates overestimation.

|                  | B2GP-PLYP-D3(BJ) | B2GP-PLYP-F12-D3(BJ) | WTMSD2 | THERMO | BARRIERS | LARGE | CONF | INTERMOL | WTMSD2 | THERMO | BARRIERS | LARGE | CONF | INTERMOL |
|------------------|------------------|----------------------|--------|--------|----------|-------|------|----------|--------|--------|----------|-------|------|----------|
| VDZ              | 1.949            | -1.040               | -0.429 | -0.350 | -0.350   | 2.055 | 1.712|          |        |        |          |       |      |          |
| VDZ*             | 2.093            | -0.310               | -0.285 | -0.305 | 2.055    | 1.564 |      |          |        |        |          |       |      |          |
| VDZ**            | 0.345            | -0.310               | -0.285 | -0.339 | 0.264    | 1.015 |      |          |        |        |          |       |      |          |
| VTZ              | 0.701            | -0.458               | -0.175 | -0.460 | 0.600    | 0.781 |      |          |        |        |          |       |      |          |
| VTZ*             | 1.077            | -0.664               | -0.978 | -0.466 | 0.600    | 0.666 |      |          |        |        |          |       |      |          |
| VTZ**            | 0.235            | -0.664               | -0.978 | -0.053 | 0.067    | 0.364 |      |          |        |        |          |       |      |          |
| VIQZ             | 0.246            | -0.261               | -0.106 | 0.097  | 0.188    | 0.417 |      |          |        |        |          |       |      |          |
| VIQZ*            | 0.501            | -0.038               | -0.028 | 0.097  | 0.188    | 0.372 |      |          |        |        |          |       |      |          |
| VIQZ**           | 0.182            | -0.038               | -0.028 | 0.005  | 0.031    | 0.213 |      |          |        |        |          |       |      |          |
| V[T,Q]Z          | 0.461            | -0.170               | -0.127 | 0.038  | 0.107    | 0.623 |      |          |        |        |          |       |      |          |
| V[T,Q]Z*         | 0.638            | 0.005                | -0.028 | 0.030  | 0.107    | 0.523 |      |          |        |        |          |       |      |          |
| V[T,Q]Z**        | 0.337            | 0.005                | -0.028 | 0.139  | 0.014    | 0.141 |      |          |        |        |          |       |      |          |
| VDZ              | 0.076            | -0.022               | -0.004 | 0.002  | 0.032    | 0.068 |      |          |        |        |          |       |      |          |
| VDZ*             | 0.019            | -0.022               | -0.004 | 0.001  | 0.007    | 0.086 |      |          |        |        |          |       |      |          |
| VDZ**            | 0.042            | 0.001                | 0.001  | -0.001 | -0.023   | 0.063 |      |          |        |        |          |       |      |          |
| V(T,Q)Z          | 0.048            | 0.001                | 0.001  | -0.001 | 0.002    | 0.014 |      |          |        |        |          |       |      |          |
| V(T,Q)Z*         | 0.183            | -0.212               | -0.012 | 0.143  | 0.039    | 0.345 |      |          |        |        |          |       |      |          |
| V(T,Q)Z**        | 0.314            | -0.181               | -0.098 | -0.008 | 0.256    | 0.211 |      |          |        |        |          |       |      |          |
| V(T,Q)ZPPP       | 0.080            | -0.038               | -0.005 | -0.008 | 0.256    | 0.211 |      |          |        |        |          |       |      |          |
| V(T,Q)ZPPP*      | 0.074            | -0.181               | -0.098 | -0.013 | 0.034    | 0.212 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPP       | 0.183            | -0.212               | -0.012 | 0.143  | 0.039    | 0.345 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPP*      | 0.314            | -0.181               | -0.098 | -0.008 | 0.256    | 0.211 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPP**     | -0.228           | -0.173               | -0.030 | 0.069  | 0.034    | -0.089 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPPP     | -0.024           | -0.097               | 0.011  | 0.069  | 0.054    | -0.061 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPPP*    | -0.060           | -0.097               | 0.011  | 0.008  | 0.024    | -0.066 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPDD     | -0.016           | -0.100               | 0.011  | 0.021  | 0.011    | 0.042 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPDD*    | -0.060           | -0.084               | -0.039 | 0.019  | 0.017    | 0.026 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPPP     | -0.088           | -0.042               | 0.007  | 0.020  | 0.039    | -0.032 |      |          |        |        |          |       |      |          |
| V(T,Q)ZVPPPP*    | -0.110           | -0.036               | 0.012  | 0.003  | 0.032    | -0.122 |      |          |        |        |          |       |      |          |

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SI.3 Basis set convergence of B2GP-PLYP PT2 correlation component of Ne atom

![Graph](image)

**Figure S1**: B2GP-PLYP same-spin and opposite-spin PT2 components for neon atom with Petersson’s nZaP basis sets as a functions of $L=n$
References

(S1) Goerigk, L.; Hansen, A.; Bauer, C.; Ehrlich, S.; Najibi, A.; Grimme, S. Phys. Chem. Chem. Phys. 2017, 19, 32184-32215.