Xiamen Atomic Calculation Suite Workshop

XEDA II Tutorial

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Chapter 1 XEDA II

1.1 Input File Syntax

For the system consisting of four water molecules shown in the figure below:

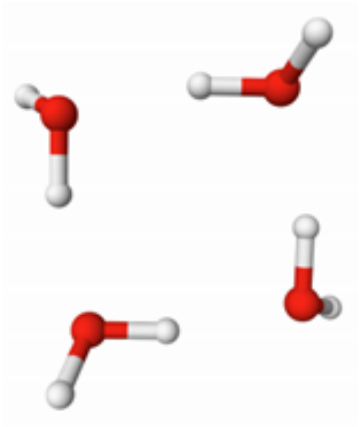

Figure 1: Interaction system of a water tetramer

We will use XEDA to calculate the intermolecular interaction energy. The input file is shown below:

```
$ctrl
method=rhf  basis=6-31g   DFT=b3lyp
type=GKS int=LR
nmul=1  charge=0
$end
$geom
O  1.2245363506 1.9369107829 -1.5249005020
H  0.6059851978 2.5732298867 -1.8865861643
H  1.1674934363 2.0403343903 -0.5520881596
O  1.4426170965 2.2936999659  1.1607557179
H  2.4102571835 2.4430589600  1.2006505497
H  1.2658427477 1.5917744265  1.7885628634
O  4.1276499342 2.6315069165  0.8942820200
H  4.5631857354 3.4690433373  1.0588206123
H  4.1895885441 2.4896149845 -0.0733228603
O  3.9157890062 2.2134800316 -1.7828881536
H  2.9430129055 2.1035712740 -1.8276494239
H  4.2809601224 1.4397383938 -2.2142395894
$end
$eda
nmol= 4
matom= 3 3 3 3
mcharge= 0 0 0 0
mmult= 1 1 1 1
$end
```

Note: Most keywords in the XEDA II input file are case-insensitive. Case-sensitive information is explicitly indicated. All other keywords are not case-sensitive.

1.1.1 $CTRL Section

This section specifies the wavefunction, basis set, functional, charge, multiplicity, and other information used in the calculation.

METHOD

- RHF

  If the spin multiplicity of the supermolecule is 1 but some monomers are open-shell molecules, XEDA will automatically use the ROHF method for the open-shell monomers.

- UHF

  XEDA II uses the UHF method for both the supermolecule and all monomers.

- ROHF

  XEDA II uses the ROHF method for the supermolecule and all monomers. (Note: currently ROHF only supports the EXACT algorithm.)

BASIS

Specifies the basis set. Currently XEDA II supports:

- STO-3G basis set
- Pople series basis sets (use * to add polarization functions and + to add diffuse functions):
  - 3-21G
  - 6-31G
  - 6-311G
- Dunning series basis sets (use the prefix aug- to add diffuse functions and the suffix -pp for pseudopotential basis sets):
  - cc-pVDZ
  - cc-pVTZ
  - cc-pVQZ
- def2 series basis sets
  - def2-SVP
  - def2-SVPP
  - def2-TZVP
  - def2-TZVPP
  - def2-QZVP
  - def2-QZVPP
  - def2-QZVPD
- Lanl2dz basis set
- SDD pseudopotential basis sets. The input format is the same as in Gaussian, but the shorthand "sdd" is not supported. The specific basis set must be specified. Examples include:

  - MDF10
  - MHF46
  - MWB28
  - SDF10
  - SHF28

- User-defined basis sets. Specify BASIS=def and provide the basis information in the $BAS section as described later.

Note: Currently the def2-PP series basis sets, pseudopotential basis sets, and user-defined basis sets only support the LR algorithm.

ECP

Specifies the pseudopotential. If a pseudopotential calculation is required, the pseudopotential must be explicitly specified, even if the chosen basis set already includes a pseudopotential (e.g., Lanl2dz). For example, one must specify ECP=lanl2dz.

Currently supported pseudopotentials include:

- Lanl2dz pseudopotential
- def2 series pseudopotentials (def2ecp)
- Dunning series pseudopotentials (cc-pvnz-pp, aug-cc-pvnz-pp)
- SDD series pseudopotentials, using the same format described above
- User-defined pseudopotentials specified with ECP=def, with detailed data provided in the $ECP section

Note: Pseudopotential calculations currently only support the LR algorithm.

DFT

Specifies the functional used in the XEDA II calculation. The supported functionals and corresponding keywords are listed below:

Functional	**Keyword**
BLYP	BLYP
B3LYP	B3LYP
B3LYP with D3 dispersion correction	B3LYP-D3
B3LYP with D3BJ dispersion correction	B3LYP-D3BJ
CAM-B3LYP	CAM-B3LYP
PBE	PBE
Hybrid PBE with 25% HF exchange	PBE0
M06-2X	M06-2X
ωB97X-D	wB97XD

TYPE

Specifies the method used in the calculation. Currently supported methods include:

- GKS

  Perform energy decomposition analysis using GKS-EDA. If TYPE is not specified, GKS is used by default.

- QMMM

  Perform QMMM calculations (see the next chapter).

- BLW

  Perform BLW-ED energy decomposition.

INT

Specifies the integral algorithm used in the calculation.

- EXACT

  Use exact electron integrals.

- LR

  Use RI-JK and RIJ-COSX methods. This algorithm is faster for large systems with large basis sets. It is particularly recommended for pure functionals (e.g., PBE, BLYP).

Note: When TYPE=GKS is specified, the default integral algorithm is EXACT if INT is not specified. When TYPE=QMMM or BLW is specified, only the LR algorithm is supported, and LR will be used by default if INT is not specified.

CHARGE

Specifies the total charge of the system.

NMUL

Specifies the total spin multiplicity of the system.

SOLVENT

Specifies the solvent type for KS-DFT calculations using the implicit solvation model.

Note: The solvent name specified by this keyword is case-sensitive and only supports the LR algorithm.

1.1.2 $GEOM Section

This section specifies the Cartesian coordinates of each atom in the molecule. The unit is Å. Element symbols in this section are **case-sensitive**.

1.1.3 $EDA Section

This section specifies the monomer information used in the EDA calculation. If this section is not provided, XEDA II performs a single-point energy calculation.

NMOL

Specifies the number of monomers.

MATOM

Specifies the number of atoms in each monomer using an array. The numbers correspond sequentially to the atoms listed in the $GEOM section.

Note: The sum of atoms in MATOM must equal the total number of atoms in the supermolecule.

MMULT

Specifies the spin multiplicity of each monomer using an array. Use + to indicate an α spin monomer and − to indicate a β spin monomer. For example, if ethane is split into two neutral methyl radicals for EDA calculation, then MMULT=2 -2 or MMULT=-2 2.

MCHARGE

Specifies the charge of each monomer using an array. The sum of all monomer charges must equal the total charge of the supermolecule.

1.1.4 $BAS Section

If BAS=def is specified in the $CTRL section, the user-defined basis set must be provided in this section.

The following formats are all valid examples:

```
$BAS
6-31G
$END
```

```
$bas
O: 6-311G*, H: 6-31G
$end
```

```
$bas
6-31G, Cu: lanl2dz
$END
```

```
$BAS
Cu:
Cu      0
S   3   1.00
        8.1760000              -0.4210260
        2.5680000               0.7385924
        0.9587000               0.5525692
S   4   1.00
        8.1760000               0.1787665
        2.5680000              -0.3592273
        0.9587000              -0.4704825
        0.1153000               1.0807407
S   1   1.00
        0.0396000               1.0000000
P   3   1.00
       25.6300000              -0.0489173
        3.1660000               0.6272854
        1.0230000               0.4716188
P   1   1.00
        0.0860000               1.0000000
```

```
P   1   1.00
        0.0240000              1.0000000
D   4   1.00
       41.3400000              0.0465424
       11.4200000              0.2227824
        3.8390000              0.4539059
        1.2300000              0.5314769
D   1   1.00
        0.3102000              1.0000000
, O: 6-31G, H: 6-31G
$end
```

```
$BAS
H     0
S   3   1.00
       18.7311370              0.03349460
        2.8253937              0.23472695
        0.6401217              0.81375733
S   1   1.00
        0.1612778              1.0000000
****
O     0
S   6   1.00
     5484.6717000              0.0018311
      825.2349500              0.0139501
      188.0469600              0.0684451
       52.9645000              0.2327143
       16.8975700              0.4701930
        5.7996353              0.3585209
SP   3   1.00
       15.5396160             -0.1107775              0.0708743
        3.5999336             -0.1480263              0.3397528
        1.0137618              1.1307670              0.7271586
SP   1   1.00
        0.2700058              1.0000000              1.0000000
****
Cu     0
S   3   1.00
        8.1760000             -0.4210260
        2.5680000              0.7385924
        0.9587000              0.5525692
S   4   1.00
        8.1760000              0.1787665
        2.5680000             -0.3592273
        0.9587000             -0.4704825
        0.1153000              1.0807407
S   1   1.00
        0.0396000              1.0000000
P   3   1.00
       25.6300000             -0.0489173
        3.1660000              0.6272854
        1.0230000              0.4716188
P   1   1.00
        0.0860000              1.0000000
P   1   1.00
        0.0240000              1.0000000
D   4   1.00
       41.3400000              0.0465424
       11.4200000              0.2227824
        3.8390000              0.4539059
        1.2300000              0.5314769
D   1   1.00
        0.3102000              1.0000000
```

```
$END
```

The formats of basis given in the 4th and 5th case follow Gaussian's format. In the 5th case, if basis data of more than 1 element should be present, four stars (****) is required to split different data of different elements.

Note: The content in the $BAS section is case-sensitive.

1.1.5 $ECP Section

If ECP=def is specified in the $CTRL section, the user-defined pseudopotential must be provided in this section.

The several following formats are legal:

```
$ECP
lanl2dz
$END
```

```
$ecp
Cu: lanl2dz, Zn: MDF10
$end
```

```
$ECP
lanl2dz, Zn: MDF10
$end
```

```
$ECP
CU     0
CU-ECP     2     10
d potential
  3
1    511.9951763            -10.0000000
2     93.2801074            -72.5548282
2     23.2206669            -12.7450231
s-d potential
  4
0    173.1180854              3.0000000
1    185.2419886             23.8351825
2     73.1517847            473.8930488
2     14.6884157            157.6345823
p-d potential
  4
0    100.7191369              5.0000000
1    130.8345665              6.4990936
2     53.8683720            351.4605395
2     14.0989469             85.5016036
$END
```

```
$ECP
CU     0
CU-ECP     2     10
d potential
  3
1    511.9951763            -10.0000000
2     93.2801074            -72.5548282
2     23.2206669            -12.7450231
```

```
s-d potential
  4
0    173.1180854              3.0000000
1    185.2419886             23.8351825
2     73.1517847            473.8930488
2     14.6884157            157.6345823
p-d potential
  4
0    100.7191369              5.0000000
1    130.8345665              6.4990936
2     53.8683720            351.4605395
2     14.0989469             85.5016036
ZN     0
ZN-ECP     3     18
f potential
  5
1    386.7379660            -18.0000000
2     72.8587359           -124.3527403
2     15.9066170            -30.6601822
2      4.3502340            -10.6358989
2      1.2842199             -0.7683623
s-f potential
  5
0     19.0867858              3.0000000
1      5.0231080             22.5234225
2      1.2701744             48.4465942
2      1.0671287            -44.5560119
2      0.9264190             12.9983958
p-f potential
  5
0     43.4927750              5.0000000
1     20.8692669             20.7435589
2     21.7118378             90.3027158
2      6.3616915             74.6610316
2      1.2291195              9.8894424
d-f potential
  3
2     13.5851800             -4.8490359
2      9.8373050              3.6913379
2      0.8373113             -0.5037319
$END
```

The formats of pseudopotential basis given in the 4th and 5th case follow Gaussian's format. In the 5th case, if basis data of more than 1 element should be present, four stars (****) is **NOT** required to split different data of different elements.

Note: The content in the $ECP section is case-sensitive.

1.2 Calculation Examples

1.2.1 Hydrogen Bond ($NH_3 \cdots H_2O$)

In this example, we use XEDA II to calculate the hydrogen-bond interaction between a water molecule and an ammonia molecule.

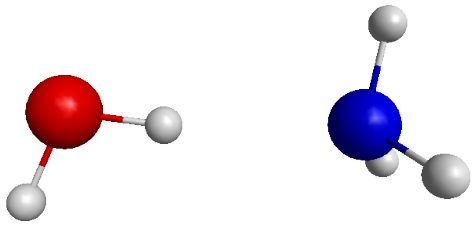

Figure 2: Hydrogen-bond interaction between water and ammonia

```
$CTRL
METHOD = RHF  BASIS = aug-cc-pvdz
NMUL = 1  CHARGE = 0
TYPE = GKS INT = EXACT
DFT = wB97XD
$END
$GEOM
N   1.37515100 -0.01976400 -0.00003700
H   1.80210900 -0.41927400  0.82476800
H   1.60816800  0.96438600 -0.01647200
H   1.80722600 -0.44771800 -0.80772500
O -1.54314600  0.10499800 -0.00000100
H -0.57947200 -0.02462600 -0.00024700
H -1.91891900 -0.77439900 -0.00006000
$END
$EDA
NMOL = 2
MATOM = 4 3
MMULT = 1 1
MCHARGE = 0 0
$END
```

The outputs are as followed.

```
 ------------------------------------------------------------------------------
 ALL BASIS SET                                    HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                ES=         -0.018752          -11.77
 EXCHANGE ENERGY                     EX=         -0.025322          -15.89
 REPULSION ENERGY                   REP=          0.045023           28.25
 POLARIZATION ENERGY                POL=         -0.007090           -4.45
 ELECTRON CORRELATION              CORR=         -0.003684           -2.31
 GRIMME DISP CORRECTION              DC=         -0.000988           -0.62
```

```
 TOTAL INTERACTION ENERGY                E=          -0.010812           -6.78
 ------------------------------------------------------------------------------
ENERGY DECOMPOSITON ANALYSIS TIME is     0.067204s
TOTAL TIME is     2.226455s
XSCF TIME:         3.26s
```

1.2.2 Covalent Bond (CH_3CH_3)

If ethane is divided into two neutral CH_3 radicals for EDA calculation, then MMULT=2 -2. The value 2 indicates that the monomer has α spin, while -2 indicates β spin.

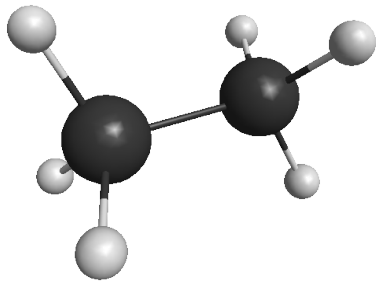

Figure 3: Covalent bond (CH_3CH_3)

```
$CTRL
METHOD=UHF BASIS=6-31G*
NMUL=1 CHARGE=0
DFT=B3LYP
TYPE=GKS INT=LR
$END
$GEOM
C     0.00000000     0.00000000     0.76766098
H    -0.51063001     0.88506198     1.16583204
H    -0.51117098    -0.88475001     1.16583204
H     1.02180099    -0.00031300     1.16583204
C     0.00000000     0.00000000    -0.76766098
H     0.51117098    -0.88475001    -1.16583204
H    -1.02180099    -0.00031300    -1.16583204
H     0.51063001     0.88506198    -1.16583204
$END
$EDA
NMOL = 2
MATOM = 4  4
MMULT = 2 -2
MCHARGE = 0  0
$END
```

The outputs:

```
 ------------------------------------------------------------------------------
 ALL BASIS SET                                        HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
```

```
 ELECTROSTATIC ENERGY                  ES=          -0.216522        -135.870
 EXCHANGE ENERGY                       EX=          -0.302654        -189.918
 REPULSION ENERGY                     REP=           0.625411         392.451
 POLARIZATION ENERGY                  POL=          -0.241558        -151.580
 ELECTRON CORRELATION                CORR=          -0.044418         -27.872
 TOTAL INTERACTION ENERGY               E=          -0.179740        -112.789
 ---------------------------------------------------------------------------
 ENERGY DECOMPOSITION ANALYSIS TIME is     0.081593s
```

1.2.3 Ionic Bond (Na^+Cl^-)

To calculate the ionic bond in Na^+Cl^-, set MCHARGE=1 -1.

```
$CTRL
METHOD=RHF BASIS=6-31+G*
NMUL=1 CHARGE=0
DFT=B3LYP
INT=LR
$END
$GEOM
Na -1.2465865600 0.4204757279 -6.0207462300
Cl -1.2465865600 2.9489348721 -6.0207462300
$END
$EDA
NMOL = 2
MATOM = 1 1
MMULT = 1 1
MCHARGE = 1 -1
$END
```

The outputs:

```
 ---------------------------------------------------------------------------
 ALL BASIS SET                                  HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                  ES=          -0.213384        -133.900
 EXCHANGE ENERGY                       EX=          -0.020552         -12.897
 REPULSION ENERGY                     REP=           0.050142          31.464
 POLARIZATION ENERGY                  POL=          -0.016494         -10.350
 ELECTRON CORRELATION                CORR=          -0.006124          -3.843
 TOTAL INTERACTION ENERGY               E=          -0.206412        -129.526
 ---------------------------------------------------------------------------
 ENERGY DECOMPOSITION ANALYSIS TIME is     0.049733s
```

1.2.4 π–π Interaction

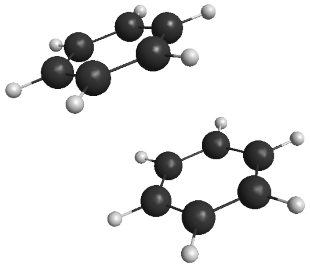

Figure 4: π–π interaction

```
$CTRL
METHOD=RHF BASIS=6-31+G*
NMUL=1 CHARGE=0
DFT=B3LYP-D3BJ
$END
$GEOM
C    0.193512806115   1.121173353129 -1.744203648026
H    0.838709129903   1.986576819171 -1.677007262072
C    0.739103211928  -0.159074248447 -1.680510912884
H    1.805821758000  -0.286922225467 -1.558001396070
C   -0.092247555773  -1.274349009792 -1.762094003120
H    0.331312130100  -2.268255027648 -1.709994478904
C   -1.468710364220  -1.109896405779 -1.905058026140
H   -2.113588214852  -1.976096050742 -1.968457910889
C   -2.014658158883   0.171228213422 -1.966290449034
H   -3.082915310030   0.299398801234 -2.078447545921
C   -1.182960120147   1.286820539326 -1.888145864186
H   -1.606033215952   2.281177856473 -1.937630565922
C    1.468627936132   1.109934852358  1.905575149948
H    2.113473059797   1.976118595545  1.969325868100
C    2.014581061727  -0.171216246872  1.967094882750
H    3.082787945798  -0.299363296881  2.079839101794
C    1.182931581883  -1.286816346390  1.888444454195
H    1.606013288989  -2.281168781877  1.938098116934
C   -0.193469979007  -1.121181317511  1.743727706167
H   -0.838572574920  -1.986591561785  1.676095073899
C   -0.739029850234   0.159051429530  1.679761877993
H   -1.805657884242   0.286880642454  1.556583117063
C    0.092247099887   1.274332191216  1.761832822027
H   -0.331277781999   2.268237225332  1.709463892086
$END
$EDA
NMOL = 2
MATOM = 12 12
MMULT = 1 1
MCHARGE = 0 0
$END
```

The outputs:

```
 ------------------------------------------------------------------------------
 ALL BASIS SET                                    HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                ES=         -0.002518           -1.58
```

```
 EXCHANGE ENERGY                        EX=          -0.016675          -10.46
 REPULSION ENERGY                      REP=           0.027025           16.96
 POLARIZATION ENERGY                   POL=          -0.001044           -0.66
 ELECTRON CORRELATION                 CORR=          -0.001868           -1.17
 GRIMME DISP CORRECTION                 DC=          -0.009312           -5.84
 TOTAL INTERACTION ENERGY                E=          -0.004393           -2.76
 ---------------------------------------------------------------------------
```

1.2.5 Interaction Calculation for an Iodine-Containing System

The following example demonstrates the calculation of the interaction energy between methyl iodide and an oxygen anion (O^-).

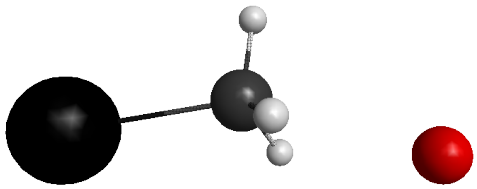

Figure 5: Calculation of interacting system consisting of I

```
$ctrl
method=uhf basis=def ecp=cc-pvnz-pp  DFT=b3lyp
nmul=2 charge=-1
int=lr
$end
$geom
 C                  1.32385600    0.39843900    0.00233500
 H                  1.85224400   -0.39327700   -0.54005500
 H                  1.43112500    1.36840900   -0.49016100
 H                  1.63924800    0.42885400    1.04753200
 I                 -0.82274400   -0.03835300   -0.00035000
 O                  3.84245800   -0.22024100   -0.00159900
$end
$eda
nmol=2
matom=5 1
mcharge=0 -1
mmult=1 2
$end
$bas
cc-pvdz, I:cc-pvdz-pp
$end
```

Outputs:

```
 ---------------------------------------------------------------------------
 ALL BASIS SET                                        HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                   ES=          -0.069800           -43.80
```

```
 EXCHANGE ENERGY                        EX=          -0.127546          -80.04
 REPULSION ENERGY                      REP=           0.220743          138.52
 POLARIZATION ENERGY                   POL=          -0.028323          -17.77
 ELECTRON CORRELATION                 CORR=          -0.022592          -14.18
 TOTAL INTERACTION ENERGY               E=          -0.027519          -17.27
 ------------------------------------------------------------------------------
```

1.2.6 Example of a User-Defined Basis Set

The following example shows the EDA calculation of the interaction energy between Cu^+ and H_2O, using a user-defined basis set and pseudopotential for Cu.

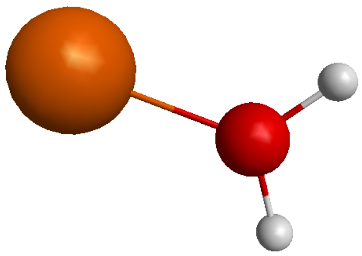

Figure 6: $Cu^+ \cdots H_2O$

```
$CTRL
method=rhf BASIS=def ecp=def DFT=wB97XD
nmul=1 CHARGE=1
INT=LR
$end
$GEOM
Cu    0.000000      0.000000      0.519295
O     0.000000     -0.000000     -1.397098
H     0.000000      0.807390     -1.941380
H    -0.000000     -0.807390     -1.941380
$end
$eda
nmoL=2
matom=1 3
Mcharge=1 0
mmult=1 1
$end
$bas
Cu:
Cu      0
S   3   1.00
       8.1760000             -0.4210260
       2.5680000              0.7385924
       0.9587000              0.5525692
S   4   1.00
       8.1760000              0.1787665
       2.5680000             -0.3592273
       0.9587000             -0.4704825
       0.1153000              1.0807407
```

```
S   1   1.00
       0.0396000              1.0000000
P   3   1.00
      25.6300000             -0.0489173
       3.1660000              0.6272854
       1.0230000              0.4716188
P   1   1.00
       0.0860000              1.0000000
P   1   1.00
       0.0240000              1.0000000
D   4   1.00
      41.3400000              0.0465424
      11.4200000              0.2227824
       3.8390000              0.4539059
       1.2300000              0.5314769
D   1   1.00
       0.3102000              1.0000000
, O: 6-31G, H: 6-31G
$end
$ecp
CU     0
CU-ECP     2     10
d potential
  3
1    511.9951763            -10.0000000
2     93.2801074            -72.5548282
2     23.2206669            -12.7450231
s-d potential
  4
0    173.1180854              3.0000000
1    185.2419886             23.8351825
2     73.1517847            473.8930488
2     14.6884157            157.6345823
p-d potential
  4
0    100.7191369              5.0000000
1    130.8345665              6.4990936
2     53.8683720            351.4605395
2     14.0989469             85.5016036
$end
```

Outputs:

```
 ---------------------------------------------------------------------------
 ALL BASIS SET                                    HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                ES=          -0.108810          -68.28
 EXCHANGE ENERGY                     EX=          -0.083442          -52.36
 REPULSION ENERGY                   REP=           0.159477          100.07
 POLARIZATION ENERGY                POL=          -0.021002          -13.18
 ELECTRON CORRELATION              CORR=          -0.022052          -13.84
 TOTAL INTERACTION ENERGY             E=          -0.075829          -47.58
 ---------------------------------------------------------------------------
 ENERGY DECOMPOSITION ANALYSIS TIME is     0.389934s
```

1.2.7 EDA Calculation with Implicit Solvent Effects

Using the CPCM implicit solvation model, the total interaction energy is decomposed as

$$\Delta G^{\mathrm{TOT}} = \Delta G^{\mathrm{ele}} + \Delta G^{\mathrm{exrep}} + \Delta G^{\mathrm{pol}} + \Delta G^{\mathrm{desol}} + \Delta G^{\mathrm{corr/disp}} \tag{1}$$

$\Delta G^{\mathrm{desol}}$ represents the influence of the solvent environment on the interaction. In solution, not only $\Delta G^{\mathrm{desol}}$ but also the other components differ from the gas phase because the KS orbitals in the two environments are different.

```
$CTRL
METHOD=RHF BASIS=6-31G
NMUL=1 CHARGE=0
DFT=PBE0 INT=LR SOLVENT=Water
$END
$GEOM
B    -1.4930097404    -0.5082255173     0.1193861744
H    -0.2909569897    -0.6053374650     0.0759344076
H    -1.9156069781     0.5145748522    -0.3618103786
H    -2.0743035096    -1.4976304007    -0.2543430610
N    -1.8483952471    -0.3946836719     1.7286231427
H    -2.8481727853    -0.3078087733     1.8739751783
H    -1.4009475344     0.4155452940     2.1428980703
H    -1.5302644453    -1.2172120485     2.2291780163
$END
$EDA
NMOL = 2
MATOM = 4 4
MMULT = 1 1
MCHARGE = 0 0
$END
```

```
 ------------------------------------------------------------------------------
 ALL BASIS SET                                      HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                 ES=          -0.150094          -94.19
 EXCHANGE ENERGY                      EX=          -0.219722         -137.88
 REPULSION ENERGY                    REP=           0.411078          257.96
 POLARIZATION ENERGY                 POL=          -0.098140          -61.58
 ELECTRON CORRELATION               CORR=          -0.023779          -14.92
 DESOLVATION ENERGY                  SOL=          -0.004019           -2.52
 TOTAL INTERACTION ENERGY              E=          -0.084675          -53.13
 ------------------------------------------------------------------------------
 ENERGY DECOMPOSITION ANALYSIS TIME is     0.076313s
```

1.3 Exercises

1.3.1 Cation–π Interaction

Submit the following input file and examine the output.

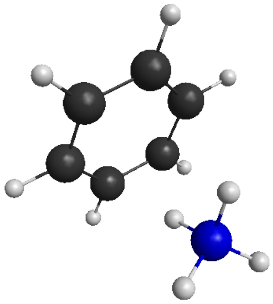

Figure 7: Cation–π interaction

```
$CTRL
METHOD=RHF BASIS=6-31G
NMUL=1 CHARGE=1
DFT=PBE
$END
$GEOM
C   0.21878885 -1.05605662   0.98621428
C  -0.71192259   1.08998501   2.54244971
C   1.13066745 -0.15188175   1.55317605
C  -1.16105485 -0.88495368   1.19366765
C  -1.62583232   0.18710911   1.97563076
C   0.66559380   0.91605544   2.33674526
H   2.19866991 -0.30624300   1.42366076
H  -1.86558342 -1.60525036   0.78568548
H  -2.69005466   0.29701740   2.16732907
H   1.37428355   1.59029782   2.81085777
H  -1.06942880   1.89622796   3.17752671
H   0.57966918 -1.90618217   0.41317517
H  -0.12747069   1.28426826  -1.57669163
N  -0.48181823   1.64109278  -0.68697900
H  -1.29492235   2.23728108  -0.85431081
H   0.24909009   2.17709398  -0.21351482
H  -0.74412972   0.84957516  -0.06764305
$END
$EDA
NMOL = 2
MATOM = 12 5
MMULT = 1 1
MCHARGE = 0 1
$END
```

Repeat the calculation using the BLYP functional and compare the results.

	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	ΔE^{pol}	ΔE^{corr}	ΔE^{TOT}
PBE						
BLYP						

Table 1: EDA components of the cation–π interaction computed with different functionals

1.3.2 Water Tetramer

Using the information below, calculate the interaction energy of the water tetramer.

Basis set: cc-pVDZ

Functional: B3LYP-D3BJ

NMOL=4

MATOM=3 3 3 3

MCHARGE=0 0 0 0

MMUL=1 1 1 1

TYPE=GKS

INT=EXACT

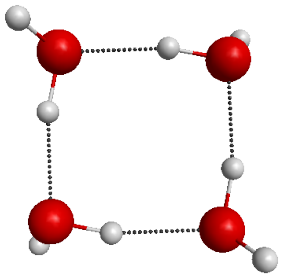

Figure 8: Interaction in a water tetramer

```
O   1.2245363506   1.9369107829  -1.5249005020
H   0.6059851978   2.5732298867  -1.8865861643
H   1.1674934363   2.0403343903  -0.5520881596
O   1.4426170965   2.2936999659   1.1607557179
H   2.4102571835   2.4430589600   1.2006505497
H   1.2658427477   1.5917744265   1.7885628634
O   4.1276499342   2.6315069165   0.8942820200
H   4.5631857354   3.4690433373   1.0588206123
H   4.1895885441   2.4896149845  -0.0733228603
O   3.9157890062   2.2134800316  -1.7828881536
H   2.9430129055   2.1035712740  -1.8276494239
H   4.2809601224   1.4397383938  -2.2142395890
```

Questions:

1. What differences exist between the interactions in a water tetramer and a water dimer?

2. How many two-body interactions exist in a water tetramer?

3. What result is obtained if the four-body interaction energy of the water tetramer subtracts all pairwise interaction energies?

Reference: Su P, Li H. J Chem Phys. 2009;131 (1): 014102

1.3.3 Base Pair (Guanine · · · Cytosine)

Using the information below, calculate the interaction energy between the guanine and cytosine base pair.

Basis set: 6-31G*

Functional: B3LYP-D3BJ

NMOL=2

MATOM=16 13

MCHARGE=0 0

MMULT=1 1

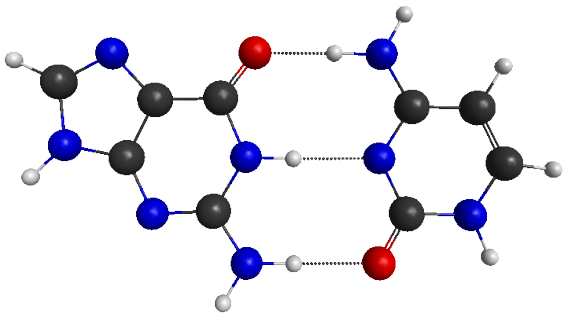

Figure 9: Guanine · · · Cytosine interaction

```
C -1.60545400 -4.76004200  0.00000000
N -0.43338800 -4.19010400  0.00000000
C -0.70709500 -2.83875700  0.00000000
C  0.15615900 -1.70395500  0.00000000
O  1.39343300 -1.67109900  0.00000000
N -0.57071300 -0.50869100  0.00000000
C -1.93515300 -0.39634200  0.00000000
N -2.43756800  0.85011000  0.00000000
N -2.74962500 -1.43773200  0.00000000
C -2.08429500 -2.60528300  0.00000000
H -1.78573000 -5.82722700  0.00000000
H  0.00000000  0.35440600  0.00000000
H -3.44059800  0.93906600  0.00000000
H -1.85217900  1.69009000  0.00000000
N -2.64385900 -3.85092400  0.00000000
H -3.63383600 -4.04644300  0.00000000
N  1.25536600  4.22216600  0.00000000
C  0.46379200  3.06706400  0.00000000
O -0.76263000  3.19975400  0.00000000
```

```
20  N   1.09991300   1.87493400   0.00000000
21  C   2.43342300   1.80377400   0.00000000
22  N   2.98731800   0.59422900   0.00000000
23  C   3.25406300   2.98666000   0.00000000
24  C   2.60993100   4.17793500   0.00000000
25  H   3.12707000   5.13194300   0.00000000
26  H   4.33581900   2.93065600   0.00000000
27  H   2.39505600  -0.25873800   0.00000000
28  H   3.98980100   0.49292400   0.00000000
29  H   0.75384100   5.09983900   0.00000000
```

Try adding the keyword INT=LR in the $CTRL section, submit the calculation, and record the computation time. Compare the time and results with those obtained using EXACT.

1.3.4 C_2H_2 Fragments

Using the information below, calculate the interaction energy between the two CH fragments in acetylene.

Basis set: cc-pVDZ

Functional: PBE0

```
1  C   0.0   -0.0    0.603523
2  H   0.0   -0.0    1.673637
3  C   0.0   -0.0   -0.603523
4  H   0.0   -0.0   -1.673637
```

1.3.5 $CO_2 \cdots CO_2$ van der Waals Interaction

Using the given geometry, write an input file and calculate the van der Waals interaction between two CO_2 molecules.

Basis set: 6-31G*

Functional: B3LYP-D3

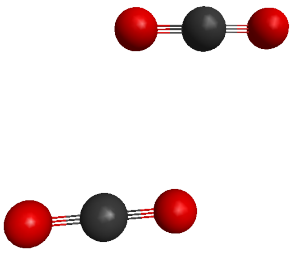

Figure 10: CO_2-CO_2 vdW interaction

```
1  C    1.0147167438    0.7851763432   -0.2899094357
2  O    1.9274594108    1.4852430742   -0.1030181813
3  O    0.0985398418    0.0867161349   -0.4812122653
4  C    0.3771707399   -2.0168042609    1.8008474122
5  O    1.3004827844   -1.3249664483    1.9816188836
6  O   -0.5429272692   -2.7100125473    1.6246407061
```

Repeat the calculation using B3LYP and compare the results with B3LYP-D3. Explain the difference.

1.3.6 Intramolecular Hydrogen-Bond Interaction

Intramolecular interactions cannot be computed strictly but can be approximated. If an intramolecular interaction system can be divided into two interacting blocks A and B (functional groups) and an environment block C, where A–C and B–C are connected by single covalent bonds, the intramolecular interaction can be approximated as

$$\Delta E_{\text{intra}}^{\text{TOT}} \approx \Delta E_{\text{ABC}}^{\text{TOT}} - \Delta E_{\text{AC}}^{\text{TOT}} - \Delta E_{\text{BC}}^{\text{TOT}} \tag{2}$$

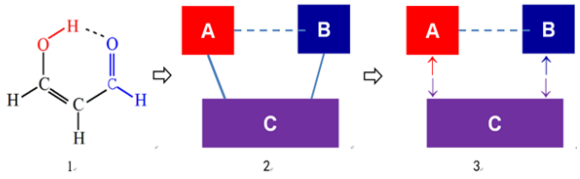

Figure 11: Intramolecular hydrogen bond

where $\Delta E_{\text{ABC}}^{\text{TOT}}$ represents the three-body interaction, $\Delta E_{\text{AC}}^{\text{TOT}}$ and $\Delta E_{\text{BC}}^{\text{TOT}}$ are tow-body interactions (In common cases, these are the binding energy of the two covalent single bonds). In the figure above, the up and down arrows represents the spin of the corresponding blocks.

The steps of calculating intramolecular interactions is listed below.

1. Calculate three-body interaction $\Delta E_{\text{ABC}}^{\text{TOT}}$
2. Calculate two-body interactions $\Delta E_{\text{AC}}^{\text{TOT}}$ and $\Delta E_{\text{BC}}^{\text{TOT}}$
3. Obtain $\Delta E_{\text{intra}}^{\text{TOT}}$ according to the formulas above.

According to the given geometry, calculate the interaction of the intramolecular hydrogen bond. Basis: 6-31G, functional: B97X-D, INT=LR

```
1  H      0.97068769     1.50898719    -0.17732553
2  O      1.91878688     1.21815002    -0.14551747
3  C      1.87280333    -0.09829685    -0.01078807
4  H      2.85514450    -0.56140238     0.03865587
5  C      0.71592110    -0.82327342     0.06110661
6  H      0.75899601    -1.89909780     0.17147529
7  C     -0.55596924    -0.14116557    -0.01149695
8  H     -1.46977472    -0.75518954     0.04966453
9  O     -0.66240388     1.08966053    -0.13794795
```

	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	ΔE^{pol}	ΔE^{corr}	ΔE^{tot}
$\Delta E^{\text{TOT}}_{\text{ABC}}$						
$\Delta E^{\text{TOT}}_{\text{AC}}$						
$\Delta E^{\text{TOT}}_{\text{BC}}$						
$\Delta E^{\text{TOT}}_{\text{intra}}$						

Table 2: Table of intramolecular hydrogen bond calculation

Reference: Su, P.*; et al. Chem. Phys. Lett. 2015, 635, 250.

http://dx.doi.org/10.1016/j.cplett.2015.06.078

1.3.7 $Cu^{2+} \cdots$ Imidazole Coordination Interaction with Pseudopotentials

Using the following geometry, calculate the $Cu^{2+} \cdots$ imidazole coordination interaction.

Basis set: Cu: lanl2dz; other elements: 6-31G

Pseudopotential: lanl2dz

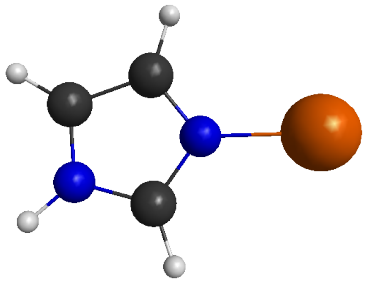

Figure 12: $Cu^{2+} \cdots$ Imidazole complex

```
C       9.7086844169   4.6857796025   2.9483153631
N      10.3377423935   3.5427750874   2.7210071309
C       8.9465432793   4.5700957516   4.1849458407
C      10.0148127351   2.7128791397   3.7450628033
N       9.1743650413   3.3513328454   4.6180573592
H       8.3178343141   5.2898397409   4.6830686904
H      10.3517458899   1.7001024251   3.8798736242
H       8.7928432938   2.9347502915   5.4666937376
H       9.7626269483   5.5512179684   2.3115357519
Cu     11.5064998878   3.1225537474   1.2067957685
```

If the Cu atom is changed from Cu^{2+} to Cu^{+}, how do the input file and calculation results change?

1.3.8 Open Exercise

Fe–Porphyrin–CO Coordination Interaction

Using the given geometry, choose a relatively small basis set, functional, and appropriate pseudopotential to perform an energy decomposition calculation for the Fe–porphyrin–CO coordination interaction.

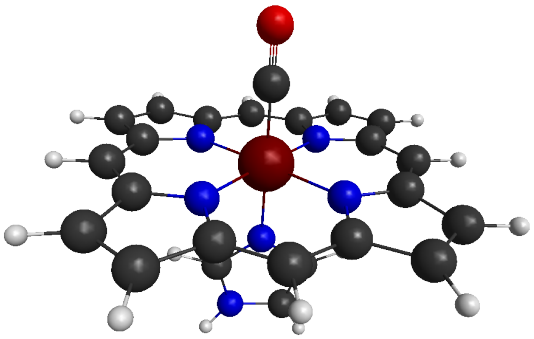

Figure 13: Fe–porphyrin–CO coordination interaction

1	C	1.07457602	0.00153900	2.40767694
2	C	-0.66392797	0.00256300	3.78807998
3	C	-1.09427595	0.00149300	2.48807406
4	N	-0.00319800	0.00099700	1.64574504
5	H	2.09176707	0.00124800	2.05338597
6	H	1.35262406	0.00321700	4.49815512
7	H	-1.19965100	0.00328000	4.72057199
8	H	-2.09844494	0.00111500	2.10035896
9	N	0.71595198	0.00256600	3.71708488
10	Fe	-0.00616600	-0.00021800	-0.38498500
11	N	1.43000102	-1.42712605	-0.35285401
12	N	-1.43864202	1.42668402	-0.34428799
13	N	1.43192005	1.42478204	-0.35435599
14	N	-1.44055295	-1.42516601	-0.34291199
15	C	2.78569889	-1.23672700	-0.41030401
16	C	1.22900796	-2.77945495	-0.27782300
17	C	3.46738291	-2.51534605	-0.36971399
18	C	2.50352311	-3.47004199	-0.28176200
19	C	-2.79405999	1.23583996	-0.39023399
20	C	-1.23750401	2.77859998	-0.27052900
21	C	-3.47619009	2.51433802	-0.34478301
22	C	-2.51241112	3.46919608	-0.26439601
23	C	2.78737211	1.23255599	-0.41143200
24	C	1.23270595	2.77740788	-0.27991599
25	C	3.47074294	2.51029205	-0.37144399
26	C	2.50812793	3.46630192	-0.28408599
27	C	-2.79572010	-1.23257005	-0.38945401
28	C	-1.24120200	-2.77731895	-0.26875299
29	C	-3.47952199	-2.51016688	-0.34379801
30	C	-2.51700592	-3.46624994	-0.26279601
31	H	4.53924799	-2.64450908	-0.40443799
32	H	2.62395000	-4.54214191	-0.22964200
33	H	-4.54839087	2.64255905	-0.36885199
34	H	-2.63264203	4.54115200	-0.20980801
35	H	4.54277992	2.63803911	-0.40610200
36	H	2.62994504	4.53827477	-0.23250900
37	H	-4.55187702	-2.63702989	-0.36818099
38	H	-2.63863111	-4.53803205	-0.20789100
39	C	-0.00199200	3.40970492	-0.23017700

```
40  C        -3.43098211     0.00204400    -0.42948401
41  C        -0.00653800    -3.41006994    -0.22790299
42  C         3.42266393    -0.00253800    -0.45396999
43  H        -0.00126400     4.49340010    -0.17418800
44  H        -4.51543808     0.00276800    -0.46512699
45  H        -0.00729400    -4.49374199    -0.17149800
46  H         4.50681496    -0.00330600    -0.49963501
47  C        -0.01110700    -0.00146200    -2.20467496
48  O        -0.01471400    -0.00242100    -3.36278892
```

S66 set

Users may click the link to download S66 testing set. You are free to choose the molecules and do EDA calculation by small basis and functions.

Chapter 2　XEDA II(QM/MM-EDA)

2.1 Input File Syntax

The input file for DM-EDA(QM/MM) is largely consistent with that used for DM-EDA calculations, but there are differences in the following sections.

2.1.1 $CTRL Section

In the $CTRL section, nearly the same keywords can be used to specify the charge, basis set, functional, multiplicity, and other information for the QM region. In addition, the keyword TYPE=QMMM must be explicitly specified.

2.1.2 $QMMM Section

In the DM-EDA(QM/MM) input file, the $GEOM section is no longer used to define molecular coordinates. Instead, the $QMMM section is used to specify the molecular structure, force field parameters, and other information related to the QM/MM calculation. The required keywords are as follows.

PDBFILE

Specifies a pdb file describing the molecular structure. The file can be uploaded via the Additional auxiliary file function.

Note: The filename specified by this keyword is case-sensitive.

XMLFILES

Specifies OpenMM-format force field parameter xml files. These files can be uploaded via the Additional auxiliary file function. If the required force field files are built-in OpenMM parameter files, they can be directly specified without uploading, such as amber14-all.xml, amber14/tip3p.xml, etc.

Note: The filenames specified by this keyword are case-sensitive.

QMATOMS

Specifies the atom indices of the QM region, starting from index 0. The selection should follow the general principles used in QM/MM methods, i.e., avoid cutting chemical bonds across the QM/MM boundary whenever possible. If bond cutting is necessary in protein or nucleic acid systems, carbon–carbon bonds should be preferred.

2.1.3 $EDA Section

In the $EDA section, the same keywords can be used to specify the number of atoms in the two interacting fragments, as well as the charge and multiplicity of each QM region. Currently, DM-EDA (QM/MM) only supports energy decomposition analysis for interactions between two fragments. If the $EDA section is not provided in the input file, the program will perform a single-point QM/MM calculation.

2.2 Calculation Examples

2.2.1 QM/MM Analysis of a Water Cluster

In this example, a cluster consisting of 1436 water molecules (water_cluster.pdb) is used for DM-EDA(QM/MM) analysis.

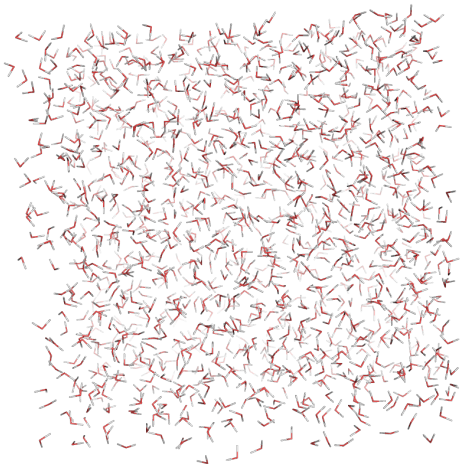

Figure 14: Schematic illustration of the water cluster

The content of the input file is as follows:

```
$ctrl
method=rhf basis=def2-svp  DFT=b3lyp-d3
nmul=1 charge=0
type=qmmm
$end
$qmmm
pdbfile=water_cluster.pdb
xmlfiles=amber14-all.xml amber14/tip3p.xml
qmatoms=1518 1519 1520 1620 1621 1622 2898 2899 2900 2913 2914 2915 3378 3379 3380
     3591 3592 3593 4305 4306 4307
$end
$eda
nmol=2
matom=4305 3
mcharge=0 0
mmult=1 1
$end
```

The output results are as follows

```
 ------------------------------------------------------------------
 QM/MM EDA RESULTS
 ------------------------------------------------------------------------------
 ALL BASIS SET                                    HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY              ES=            -0.026951          -16.91
 EXCHANGE ENERGY                   EX=            -0.055236          -34.66
```

```
 REPULSION ENERGY                  REP=              0.094081          59.04
 POLARIZATION ENERGY               POL=             -0.002174          -1.36
 ELECTRON CORRELATION             CORR=             -0.014039          -8.81
 TOTAL INTERACTION ENERGY            E=             -0.004318          -2.71
 ------------------------------------------------------------------------------

 ------------ENDING QM/MM EDA-------------
```

2.2.2 Protein–Ligand Interaction

In this example, a protein–small-molecule complex structure file (complex.pdb) is used for DM-EDA(QM/MM) analysis.

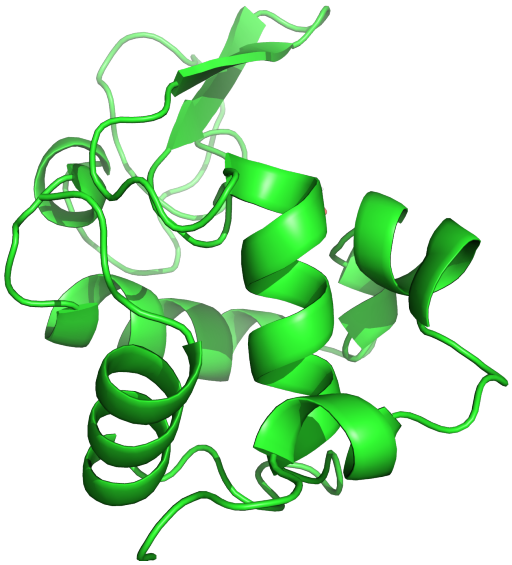

Figure 15: Schematic illustration of the protein–ligand complex

The content of the input file is as follows:

```
$ctrl
method=rhf basis=def2-svp  DFT=b3lyp-d3
nmul=1 charge=1
type=qmmm
$end
$qmmm
pdbfile=complex.pdb
xmlfiles=amber14-all.xml amber14/tip3p.xml openff_LIG.xml
qmatoms=890 891 892 893 896 897 898 899 913 914 915 916 917 918 919 920 921 924
    925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943
    944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 963 964
    965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 1465
    1466 1467 1468 1471 1472 1473 1474 1475 1476 1477 1478 1479 1580 1581 1582
    1585 1586 1587 1588 1589 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601
    1602 1603 1604 1605 1606 1607 1608 1609 1610 1611 1960 1961 1962 1963 1964
    1965
$end
$eda
nmol=2
matom=1960 6
```

```
mcharge=1 0
mmult=1 1
$end
```

The output results are as follows

```
 ------------------------------------------------------------------
 QM/MM EDA RESULTS
 ------------------------------------------------------------------------------
 ALL BASIS SET                                      HARTREE          KCAL/MOL
 ------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY              ES=               0.001485            0.93
 EXCHANGE ENERGY                   EX=              -0.052266          -32.80
 REPULSION ENERGY                 REP=               0.090053           56.51
 POLARIZATION ENERGY              POL=               0.004694            2.95
 ELECTRON CORRELATION            CORR=              -0.039860          -25.01
 TOTAL INTERACTION ENERGY           E=               0.004106            2.58
 ------------------------------------------------------------------------------

 ------------ENDING QM/MM EDA-------------
```

2.2.3 Interaction Between Two Peptide Chains

In this example, a double-chain peptide structure file (di_asp_opt.pdb) is used for DM-EDA(QM/MM) analysis.

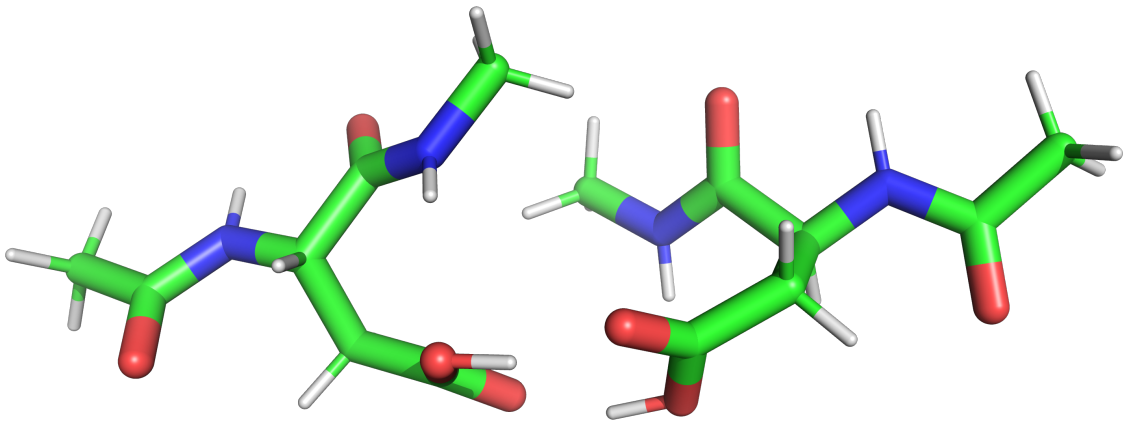

Figure 16: Schematic illustration of two peptide chains

The content of the input file is as follows:

```
$ctrl
method=rhf basis=def2-svp  DFT=b3lyp-d3
nmul=1 charge=0
type=qmmm
$end
$qmmm
```

```
pdbfile=di_asp_opt.pdb
xmlfiles=amber14-all.xml amber14/tip3p.xml
qmatoms=10 11 12 13 16 17 18 35 36 37 38 41 42 43
$end
$eda
nmol=2
matom=25 25
mcharge=0 0
mmult=1 1
$end
```

The output results are as follows

```
 ---------------------------------------------------------------------
 QM/MM EDA RESULTS
 ---------------------------------------------------------------------------------------
 ALL BASIS SET                                        HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------------------
 ELECTROSTATIC ENERGY              ES=               -0.071439          -44.83
 EXCHANGE ENERGY                   EX=               -0.100799          -63.25
 REPULSION ENERGY                 REP=                0.187046          117.37
 POLARIZATION ENERGY              POL=               -0.038775          -24.33
 ELECTRON CORRELATION            CORR=               -0.018377          -11.53
 TOTAL INTERACTION ENERGY           E=               -0.042345          -26.57
 ---------------------------------------------------------------------------------------

 ------------ENDING QM/MM EDA-------------
```

2.2.4 Interaction Between a Metal Ion and a Protein

In this example, a copper protein structure file (2cak.pdb) is used for DM-EDA(QM/MM) analysis.

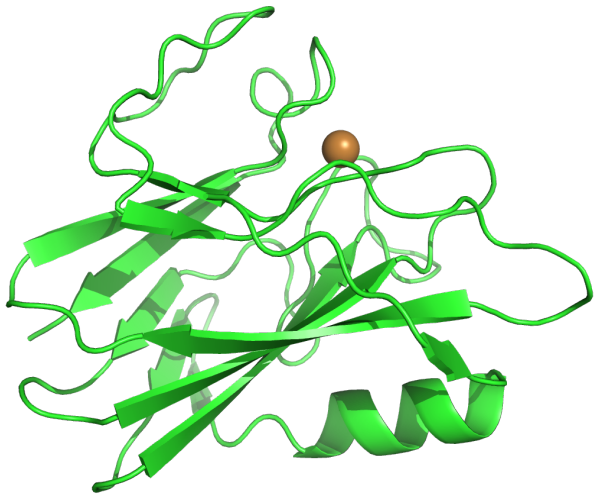

Figure 17: Schematic structure of the copper protein (PDBID:2CAK)

The content of the input file is as follows:

```
$ctrl
method=rhf basis=def2-svp  DFT=b3lyp-d3
```

```
nmul=1 charge=1
type=qmmm
$end
$qmmm
pdbfile=2cak-fix.pdb
xmlfiles=amber14-all.xml amber14/tip3p.xml ./cu-ion.xml
qmatoms=759 760 761 762 763 764 1216 1217 1218 1219 1220 1221 1222 1223 1224 1225
    1226 1227 1228 1229 1241 1242 1243 1244 1245 1246 1247 1248 1249 1250 1251
    1252 1253 1254 1255 1256 1257 1260 1261 1262 1263 1264 2056 2057 2058 2059
    2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074
    2075 2076 2077 2078 2079 2080 2081 2082 2083 2086 2087 2088 2089 2090 2091
    2092 2093 2094 2095 2096 2097 2098 2126 2127 2128 2129 2130 2131 2132 2133
    2134 2135 2136 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2321
$end
$eda
nmol=2
matom=2321 1
mcharge=0 1
mmult=1 1
$end
```

The output results are as follows

```
-------------------------------------------------------------------------
QM/MM EDA RESULTS
-------------------------------------------------------------------------------
ALL BASIS SET                                      HARTREE          KCAL/MOL
-------------------------------------------------------------------------------
ELECTROSTATIC ENERGY              ES=              -0.225173         -141.30
EXCHANGE ENERGY                   EX=              -0.212264         -133.20
REPULSION ENERGY                 REP=               0.443943          278.58
POLARIZATION ENERGY              POL=              -0.089397          -56.10
ELECTRON CORRELATION            CORR=              -0.112135          -70.37
TOTAL INTERACTION ENERGY           E=              -0.195027         -122.38
-------------------------------------------------------------------------------

------------ENDING QM/MM EDA-------------
```

Chapter 3 Appendix

3.1 Answer To The Exercises

3.1.1 1.3.1 Cation-π Interaction

PBE

```
1  ------------------------------------------------------------------------------
2  ALL BASIS SET                                      HARTREE          KCAL/MOL
3  ------------------------------------------------------------------------------
4  ELECTROSTATIC ENERGY                 ES=          -0.023751          -14.90
5  EXCHANGE ENERGY                      EX=          -0.022623          -14.20
6  REPULSION ENERGY                    REP=           0.043651           27.39
7  POLARIZATION ENERGY                 POL=          -0.017251          -10.83
8  ELECTRON CORRELATION               CORR=          -0.007429           -4.66
9  GRIMME DISP CORRECTION               DC=           0.000000            0.00
10 TOTAL INTERACTION ENERGY              E=          -0.027402          -17.20
11 ------------------------------------------------------------------------------
```

BLYP

```
1  ------------------------------------------------------------------------------
2  ALL BASIS SET                                      HARTREE          KCAL/MOL
3  ------------------------------------------------------------------------------
4  ELECTROSTATIC ENERGY                 ES=          -0.022786          -14.30
5  EXCHANGE ENERGY                      EX=          -0.023682          -14.86
6  REPULSION ENERGY                    REP=           0.045426           28.51
7  POLARIZATION ENERGY                 POL=          -0.018468          -11.59
8  ELECTRON CORRELATION               CORR=          -0.003469           -2.18
9  GRIMME DISP CORRECTION               DC=           0.000000            0.00
10 TOTAL INTERACTION ENERGY              E=          -0.022981          -14.42
11 ------------------------------------------------------------------------------
```

3.1.2 1.3.2 Water Tetramer

```
1  ------------------------------------------------------------------------------
2  ALL BASIS SET                                      HARTREE          KCAL/MOL
3  ------------------------------------------------------------------------------
4  ELECTROSTATIC ENERGY                 ES=          -0.092813          -58.24
5  EXCHANGE ENERGY                      EX=          -0.138797          -87.10
6  REPULSION ENERGY                    REP=           0.245976          154.35
7  POLARIZATION ENERGY                 POL=          -0.042420          -26.62
8  ELECTRON CORRELATION               CORR=          -0.016778          -10.53
9  GRIMME DISP CORRECTION               DC=          -0.005389           -3.38
10 TOTAL INTERACTION ENERGY              E=          -0.050221          -31.51
11 ------------------------------------------------------------------------------
```

3.1.3 1.3.3 Base Pair (Guanine $\cdots$ Cytosine)

EXACT

```
1  ------------------------------------------------------------------------------
2  ALL BASIS SET                                      HARTREE          KCAL/MOL
3  ------------------------------------------------------------------------------
4  ELECTROSTATIC ENERGY                 ES=          -0.079119          -49.65
5  EXCHANGE ENERGY                      EX=          -0.102636          -64.41
6  REPULSION ENERGY                    REP=           0.184022          115.48
```

POLARIZATION ENERGY	POL=	-0.042223	-26.50
ELECTRON CORRELATION	CORR=	-0.006792	-4.26
GRIMME DISP CORRECTION	DC=	-0.008304	-5.21
TOTAL INTERACTION ENERGY	E=	-0.055053	-34.55

LR

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.079097	-49.63
EXCHANGE ENERGY	EX=	-0.102619	-64.39
REPULSION ENERGY	REP=	0.184025	115.48
POLARIZATION ENERGY	POL=	-0.042217	-26.49
ELECTRON CORRELATION	CORR=	-0.015421	-9.68
TOTAL INTERACTION ENERGY	E=	-0.055330	-34.72

3.1.4 1.3.4 C_2H_2 Fragments

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.713833	-447.94
EXCHANGE ENERGY	EX=	-1.068786	-670.67
REPULSION ENERGY	REP=	3.139032	1969.77
POLARIZATION ENERGY	POL=	-1.642393	-1030.62
ELECTRON CORRELATION	CORR=	-0.094074	-59.03
GRIMME DISP CORRECTION	DC=	0.000000	0.00
TOTAL INTERACTION ENERGY	E=	-0.380054	-238.49

3.1.5 1.3.5 $CO_2 \cdots CO_2$ van der Waals Interaction

B3LYP-D3

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.002828	-1.77
EXCHANGE ENERGY	EX=	-0.004709	-2.95
REPULSION ENERGY	REP=	0.008185	5.14
POLARIZATION ENERGY	POL=	-0.000986	-0.62
ELECTRON CORRELATION	CORR=	-0.002099	-1.32
TOTAL INTERACTION ENERGY	E=	-0.002437	-1.53

B3LYP

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.002828	-1.77
EXCHANGE ENERGY	EX=	-0.004709	-2.95
REPULSION ENERGY	REP=	0.008183	5.13

```
 POLARIZATION ENERGY                  POL=          -0.000984           -0.62
 ELECTRON CORRELATION                CORR=           0.000054            0.03
 TOTAL INTERACTION ENERGY              E=          -0.000284           -0.18
 ---------------------------------------------------------------------------
```

3.1.6 1.3.6 Intramolecular Hydrogen-Bond Interaction

	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	ΔE^{pol}	ΔE^{corr}	ΔE^{tot}
$\Delta E^{\text{TOT}}_{\text{ABC}}$	-464.71	-693.62	1649.56	-657.21	-70.60	-236.58
$\Delta E^{\text{TOT}}_{\text{AC}}$	-262.06	-401.08	1024.13	-427.74	-44.61	-111.36
$\Delta E^{\text{TOT}}_{\text{BC}}$	-190.68	-265.76	577.83	-217.09	-19.41	-115.11
$\Delta E^{\text{TOT}}_{\text{intra}}$	-11.97	-26.78	47.6	-12.38	-6.58	-10.11

Table 3: (kcal/mol)

3.1.7 1.3.7 $Cu^{2+} \cdots$ Imidazole Coordination Interaction with Pseudopotentials

Cu^2+

```
 ---------------------------------------------------------------------------
 ALL BASIS SET                                HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                  ES=          -0.208217         -130.66
 EXCHANGE ENERGY                       EX=          -0.068879          -43.22
 REPULSION ENERGY                     REP=           0.166293          104.35
 POLARIZATION ENERGY                  POL=          -0.196318         -123.19
 ELECTRON CORRELATION                CORR=          -0.078025          -48.96
 TOTAL INTERACTION ENERGY              E=          -0.385146         -241.68
 ---------------------------------------------------------------------------
```

Cu^+

```
 ---------------------------------------------------------------------------
 ALL BASIS SET                                HARTREE          KCAL/MOL
 ---------------------------------------------------------------------------
 ELECTROSTATIC ENERGY                  ES=          -0.146877          -92.17
 EXCHANGE ENERGY                       EX=          -0.092640          -58.13
 REPULSION ENERGY                     REP=           0.192480          120.78
 POLARIZATION ENERGY                  POL=          -0.040175          -25.21
 ELECTRON CORRELATION                CORR=          -0.032814          -20.59
 TOTAL INTERACTION ENERGY              E=          -0.120026          -75.32
 ---------------------------------------------------------------------------
```

3.2 Partial Keywords Details

3.2.1 Supporting SDD Pseudopotential Basis Sets

Table 4: Name and Supporting Elements of SDD Series

ECP	Supporting Elements
MDF10	As, Br, Ca, Co, Cr, Cu, Fe, Ga, Ge, K, Kr, Mn, Ni, Sc, Se, Ti, V, Zn
MDF28	Ag, As, Br, Cd, Ge, I, In, Mo, Nb, Pd, Rb, Rh, Ru, Sb, Se, Sn, Sr, Tc, Te, Xe, Y, Zr
MDF46	Ba, Cs, I, Sb, Sn, Te
MDF60	Ac, At, Au, Bi, Hf, Hg, Ir, Os, Pa, Pb, Po, Pt, Re, Rn, Ta, Th, Tl, U, W, Yb
MDF68	Yb
MDF78	At, Bi, Fr, Pb, Po, Ra
MDFB92	Cn, Fl, Lv
MDFQ92	Cn, Fl, Lv, Rg
MHF10	Ar, Ca, Co, Cr, Cu, Fe, Ga, Mn, Ni, Sc, Ti, V, Zn
MHF18	Ti
MHF2	Ne
MHF28	Ag, Cd, Ce, Dy, Er, Eu, Gd, Ho, In, Kr, Mo, Nb, Nd, Pd, Pm, Pr, Rh, Ru, Sm, Sr, Tb, Tc, Tm, Y, Yb, Zr
MHF46	Ba, La, Xe
MHF47	Ce, La
MHF48	Ce, Pr
MHF49	Nd, Pr
MHF50	Nd, Pm
MHF51	Pm, Sm
MHF52	Eu, Sm
MHF53	Eu, Gd
MHF54	Gd, Tb
MHF55	Dy, Tb
MHF56	Dy, Ho
MHF57	Er, Ho
MHF58	Er, Tm
MHF59	Tm, Yb
MHF60	Ac, Am, Au, Bk, Cf, Cm, Es, Fm, Hf, Hg, Ir, Lr, Lu, Md, No, Np, Os, Pa, Pt, Pu, Re, Ta, Th, Tl, U, W, Yb
MHF78	At, Bi, Hg, Pb, Po, Rn, Tl
MWB10	Al, Ar, Ca, Cl, Cu, Ga, K, P, S, Si, Zn

ECP	Supporting Elements
MWB18	Ga
MWB2	C, F, N, Ne, O
MWB28	Ag, As, Br, Cd, Ce, Dy, Er, Eu, Ga, Gd, Ge, Ho, In, Kr, La, Lu, Mo, Nb, Nd, Pd, Pm, Pr, Rb, Rh, Ru, Se, Sm, Sr, Tb, Tc, Tm, Y, Yb, Zn, Zr
MWB36	In
MWB46	Ba, Cd, Ce, Cs, I, In, La, Sb, Sn, Te, Xe
MWB47	Ce, La, Pr
MWB48	Ce, Nd, Pr
MWB49	Nd, Pr
MWB50	Nd, Pm
MWB51	Pm, Sm
MWB52	Eu, Sm
MWB53	Eu, Gd, Tb
MWB54	Dy, Gd, Tb
MWB55	Dy, Tb
MWB56	Dy, Ho
MWB57	Er, Ho
MWB58	Er, Tm
MWB59	Tm, Yb
MWB60	Ac, Am, Au, Bk, Cf, Cm, Es, Fm, Hf, Hg, Ir, Lr, Lu, Md, No, Np, Os, Pa, Pt, Pu, Re, Ta, Th, Tl, U, W, Yb
MWB68	Tl
MWB78	Ac, At, Bi, Hg, Pa, Pb, Po, Rn, Th, Tl, U
MWB79	Pa, Th, U
MWB80	Np, Pa, U
MWB81	Np, Pu, U
MWB82	Am, Np, Pu
MWB83	Am, Pu
MWB84	Am, Cm, Pu
MWB85	Am, Bk, Cm
MWB86	Bk, Cf, Cm
MWB87	Bk, Cf
MWB88	Cf, Es
MWB89	Es, Fm
MWB90	Fm, Md
MWB91	Md, No
MWB92	Lr, No
SDF10	Al, Cl, Mg, Na, P, S, Si

ECP	Supporting Elements
SDF18	Ca, K
SDF2	C, F, N, O
SDF28	As, Br, Cu, Ga, Ge, Se, Zn
SDF36	Rb, Sr
SDF46	Ag, Cd, I, In, Sb, Sn, Te
SDF54	Ba, Cs
SDF78	Au
SHF18	Ca, K
SHF28	Cu, Ge
SHF36	Rb, Sr
SHF46	Ag
SHF54	Cs
SHF78	Au

3.2.2 Supporting Solvent

Table 5: Name and Dielectric Constant

Solvent	Dielectric constant	Solvent	Dielectric constant
Water	78.3553	Butanone	18.246
Acetonitrile	35.688	ButanoNitrile	24.291
Methanol	32.613	ButylAmine	4.6178
Ethanol	24.852	ButylEthanoate	4.9941
IsoQuinoline	11.0	CarbonDiSulfide	2.6105
Quinoline	9.16	Cis-1,2-DiMethylCycloHexane	2.06
Chloroform	4.7113	Cis-Decalin	2.2139
DiethylEther	4.24	CycloHexanone	15.619
Dichloromethane	8.93	CycloPentane	1.9608
DiChloroEthane	10.125	CycloPentanol	16.989
CarbonTetraChloride	2.228	CycloPentanone	13.58
Benzene	2.2706	Decalin-mixture	2.196
Toluene	2.3741	DiBromomEthane	7.2273
ChloroBenzene	5.6968	DiButylEther	3.0473
NitroMethane	36.562	DiEthylAmine	3.5766
Heptane	1.9113	DiEthylSulfide	5.723
CycloHexane	2.0165	DiIodoMethane	5.32
Aniline	6.8882	DiIsoPropylEther	3.38
Acetone	20.493	DiMethylDiSulfide	9.6

Solvent	Dielectric constant	Solvent	Dielectric constant
TetraHydroFuran	7.4257	DiPhenylEther	3.73
DiMethylSulfoxide	46.826	DiPropylAmine	2.9112
Argon	1.43	e-1,2-DiChloroEthene	2.14
Krypton	1.519	e-2-Pentene	2.051
Xenon	1.706	EthaneThiol	6.667
n-Octanol	9.8629	EthylBenzene	2.4339
1,1,1-TriChloroEthane	7.0826	EthylEthanoate	5.9867
1,1,2-TriChloroEthane	7.1937	EthylMethanoate	8.331
1,2,4-TriMethylBenzene	2.3653	EthylPhenylEther	4.1797
1,2-DiBromoEthane	4.9313	FluoroBenzene	5.42
1,2-EthaneDiol	40.245	Formamide	108.94
1,4-Dioxane	2.2099	FormicAcid	51.1
1-Bromo-2-MethylPropane	7.7792	HexanoicAcid	2.6
1-BromoOctane	5.0244	IodoBenzene	4.547
1-BromoPentane	6.269	IodoEthane	7.6177
1-BromoPropane	8.0496	IodoMethane	6.865
1-Butanol	17.332	IsoPropylBenzene	2.3712
1-ChloroHexane	5.9491	m-Cresol	12.44
1-ChloroPentane	6.5022	Mesitylene	2.265
1-ChloroPropane	8.3548	MethylBenzoate	6.7367
1-Decanol	7.5305	MethylButanoate	5.5607
1-FluoroOctane	3.89	MethylCycloHexane	2.024
1-Heptanol	11.321	MethylEthanoate	6.8615
1-Hexanol	12.51	MethylMethanoate	8.8377
1-Hexene	2.0717	MethylPropanoate	6.0777
1-Hexyne	2.615	m-Xylene	2.3478
1-IodoButane	6.173	n-ButylBenzene	2.36
1-IodoHexaDecane	3.5338	n-Decane	1.9846
1-IodoPentane	5.6973	n-Dodecane	2.006
1-IodoPropane	6.9626	n-Hexadecane	2.0402
1-NitroPropane	23.73	n-Hexane	1.8819
1-Nonanol	8.5991	NitroBenzene	34.809
1-Pentanol	15.13	NitroEthane	28.29
1-Pentene	1.9905	n-MethylAniline	5.96
1-Propanol	20.524	n-MethylFormamide-mixture	181.56
2,2,2-TriFluoroEthanol	26.726	n,n-DiMethylAcetamide	37.781
2,2,4-TriMethylPentane	1.9358	n,n-DiMethylFormamide	37.219
2,4-DiMethylPentane	1.8939	n-Nonane	1.9605

Solvent	Dielectric constant	Solvent	Dielectric constant
2,4-DiMethylPyridine	9.4176	n-Octane	1.9406
2,6-DiMethylPyridine	7.1735	n-Pentadecane	2.0333
2-BromoPropane	9.361	n-Pentane	1.8371
2-Butanol	15.944	n-Undecane	1.991
2-ChloroButane	8.393	o-ChloroToluene	4.6331
2-Heptanone	11.658	o-Cresol	6.76
2-Hexanone	14.136	o-DiChloroBenzene	9.9949
2-MethoxyEthanol	17.2	o-NitroToluene	25.669
2-Methyl-1-Propanol	16.777	o-Xylene	2.5454
2-Methyl-2-Propanol	12.47	Pentanal	10.0
2-MethylPentane	1.89	PentanoicAcid	2.6924
2-MethylPyridine	9.9533	PentylAmine	4.201
2-NitroPropane	25.654	PentylEthanoate	4.7297
2-Octanone	9.4678	PerFluoroBenzene	2.029
2-Pentanone	15.2	p-IsoPropylToluene	2.2322
2-Propanol	19.264	Propanal	18.5
2-Propen-1-ol	19.011	PropanoicAcid	3.44
3-MethylPyridine	11.645	PropanoNitrile	29.324
3-Pentanone	16.78	PropylAmine	4.9912
4-Heptanone	12.257	PropylEthanoate	5.5205
4-Methyl-2-Pentanone	12.887	p-Xylene	2.2705
4-MethylPyridine	11.957	Pyridine	12.978
5-Nonanone	10.6	sec-ButylBenzene	2.3446
AceticAcid	6.2528	tert-ButylBenzene	2.3447
AcetoPhenone	17.44	TetraChloroEthene	2.268
a-ChloroToluene	6.7175	TetraHydroThiophene-s,s-dioxide	43.962
Anisole	4.2247	Tetralin	2.771
Benzaldehyde	18.22	Thiophene	2.727
BenzoNitrile	25.592	Thiophenol	4.2728
BenzylAlcohol	12.457	trans-Decalin	2.1781
BromoBenzene	5.3954	TriButylPhosphate	8.1781
BromoEthane	9.01	TriChloroEthene	3.422
Bromoform	4.2488	TriEthylAmine	2.3832
Butanal	13.45	Xylene-mixture	2.3879
ButanoicAcid	2.9931	z-1,2-DiChloroEthene	9.2