Distributed multipoles from a robust basis-space implementation of the iterated stockholder atoms procedure

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Supplementary Information

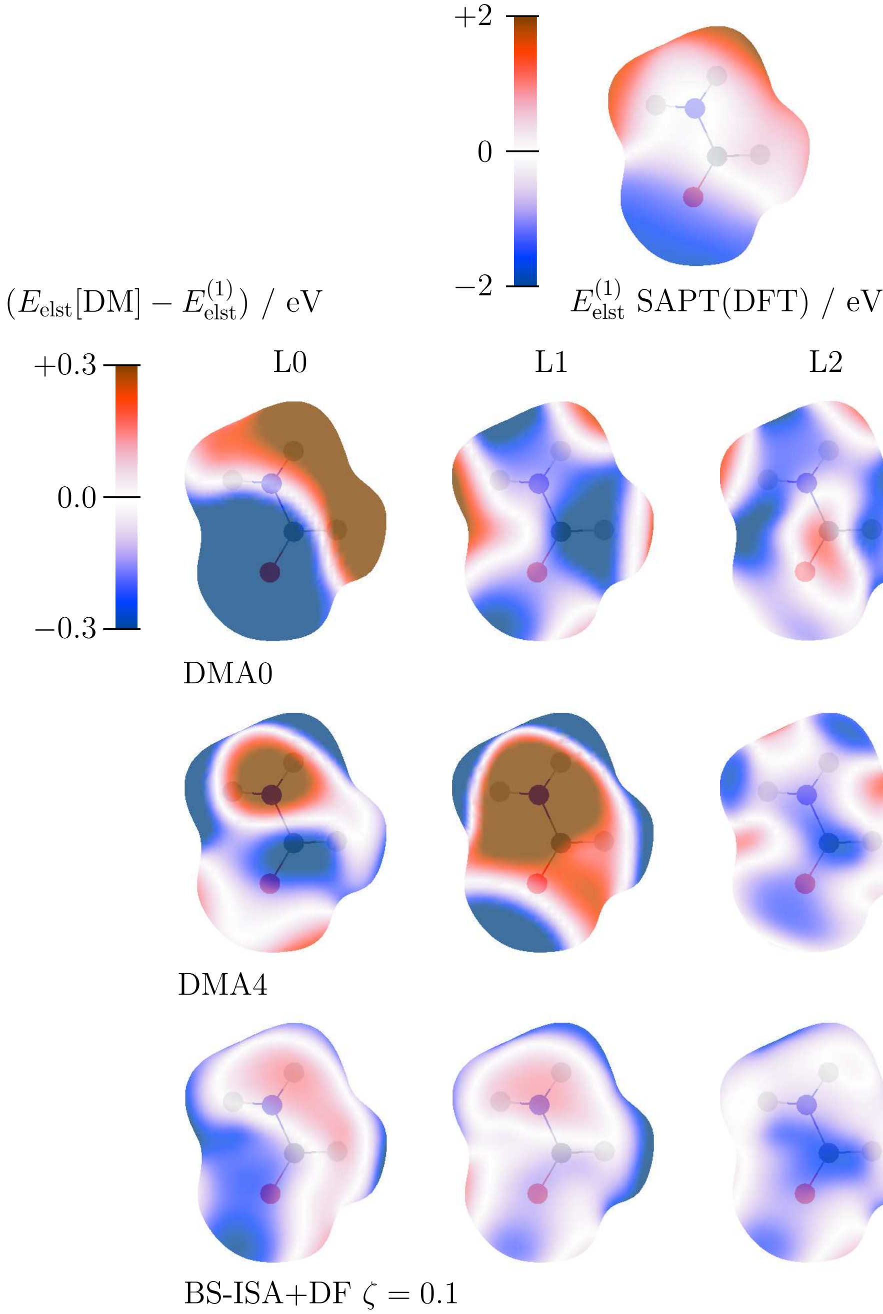

FIG. 1: Electrostatic maps of formamide with a point charge probe with charge +1 a.u. The top figure illustrates the SAPT(DFT) electrostatic energy for this system, while the rest illustrate difference maps computed against the SAPT(DFT) result using the DMA0, DMA4 and BS-ISA/ζ = 0.1 multipole moment models at various ranks. Labels Ln denote the maximum rank n of terms in the model. Results for the L3 models are not shown as they are similar to those from the L4 models.

Shown here are colour maps of $(E_{\rm elst}[\rm DM] - E^{(1)}_{\rm elst})$ plotted on the 0.001 a.u. isosurface of formamide. See the discussion in sec. IV (Multipoles) of the paper. The superior convergence pattern of the multipoles from the BS-ISA+DF method is clearly visible.

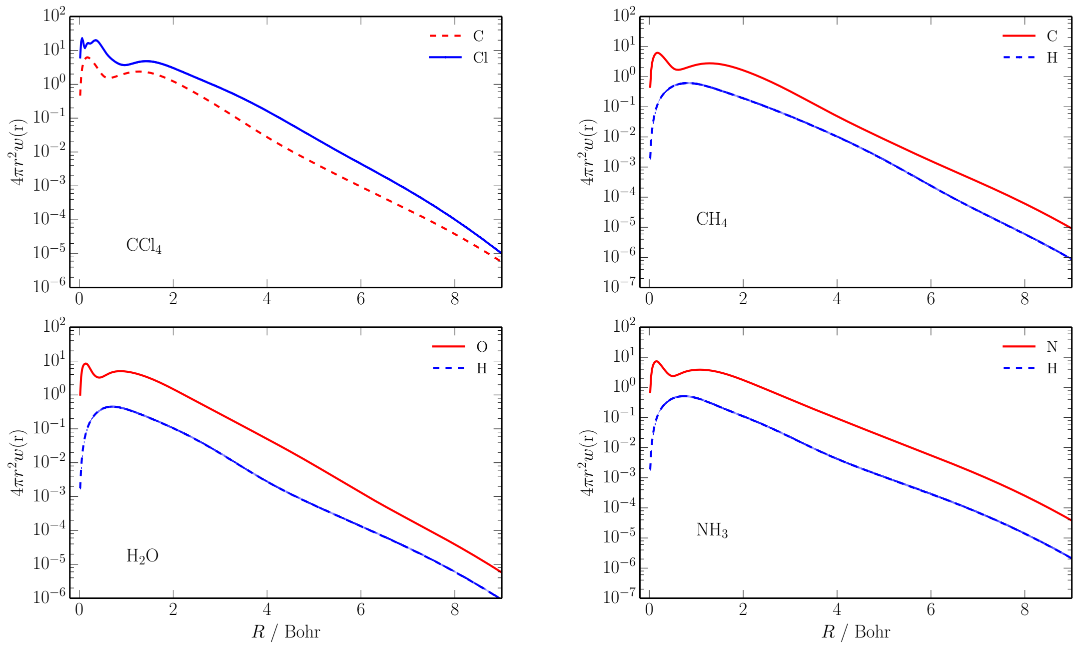

FIG. 2: BS-ISA+DF shape functions for atoms in CCl_4, CH_4, H_2O and NH_3. We have plotted $4\pi r^2 w(r)$ to better illustrate the shell structure. The aug-cc-pVQZ basis was used to calculate the density. The BS-ISA+DF calculation was performed using the aQZ/set2 basis. In the last panel carbon shape functions are compared for carbon atoms in benzene, methane and carbon tetrachloride. All shape functions were obtained using the BS-ISA+DF algorithm with $\zeta = 0.9$.

A. Shape functions

In fig. 2 we display BS-ISA+DF ($\zeta = 0.9$) shape functions for the atoms in CCl_4, CH_4, H_2O and NH_3.

B. Signed potential differences

In fig. 3 we display signed potential differences and standard deviations for LiF, H_2CO, NH_3 and benzene.

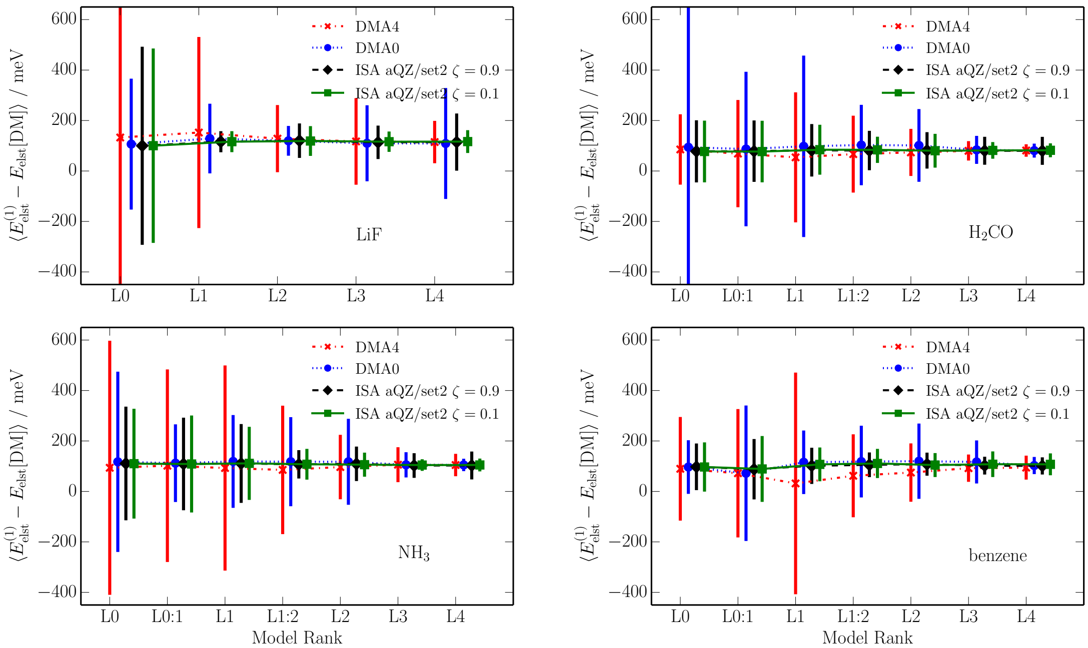

FIG. 3: Average signed potential differences and and their standard deviation calculated using a point charge probe placed on the 10^{-3} iso-surfaces of the pyridine, water, formamide and methane molecules. The DMA0, DMA4 and BS-ISA $\zeta = 0.1, 0.9$ models at various ranks are used to calculate the multipole energies. Ranks are indicated by either Ln or Ln : m. In the former case, all atoms have multipoles limited to rank n and in the latter, hydrogen atoms are limited to rank n and heavier atoms to rank m.

C. Molecular geometries and ISA moments for a selection of molecules

Unless otherwise indicated atomic units are used for all quantities. Molecular geometries are reported in XYZ format. Vertical ionisation energies used in the asymptotic correction are also provided.

BS-ISA+DF multipoles have been calculated with $\zeta = 0.1$.

Multipole moments for each site are reported in the following format:

```
ATOM       Rx       Ry       Rz      Type ATOM-TYPE  Rank RANK
    Q00
    Q10    Q11c     Q11s
    Q20    Q21c     Q21s     Q22c     Q22s
    Q30    Q31c     Q31s     Q32c     Q32s
           Q33c     Q33s
    Q40    Q41c     Q41s     Q42c     Q42s
           Q43c     Q43s     Q44c     Q44s
```

1. H_2O

```
! Multipole moments for H2O.   IP 0.4638 a.u.
! Based on DF-type : ISA

   O     0.00000000     0.00000000     0.00000000     Type    O      Rank   4
      -0.805948
       0.181288       0.000000       0.000000
      -0.054462       0.000000       0.000000       0.549633       0.000000
      -0.090145       0.000000       0.000000       0.069592       0.000000
                      0.000000       0.000000
      -0.386324       0.000000       0.000000       0.456414       0.000000
                      0.000000       0.000000       0.059674       0.000000

  H1    -1.45365196     0.00000000    -1.12168732     Type    H      Rank   4
       0.402974
      -0.008839      -0.017784       0.000000
       0.001421       0.020045       0.000000       0.010832       0.000000
      -0.006919      -0.026292       0.000000      -0.039199       0.000000
                     -0.072935       0.000000
       0.052403      -0.013113       0.000000      -0.073603       0.000000
                     -0.029012       0.000000      -0.080175       0.000000

  H2     1.45365196     0.00000000    -1.12168732     Type    H      Rank   4
       0.402974
      -0.008839       0.017783       0.000000
       0.001421      -0.020045       0.000000       0.010832       0.000000
      -0.006919       0.026292       0.000000      -0.039199       0.000000
                      0.072936       0.000000
       0.052403       0.013113       0.000000      -0.073603       0.000000
                      0.029012       0.000000      -0.080175       0.000000
```

2. H_2CO

```
! Multipole moments for H2CO.   IP  0.3998  a.u.
! Based on DF-type : ISA

  C     0.00000000     0.00000000     0.00000000     Type    C       Rank   4
      0.337166
      0.000000       0.067446       0.000000
      0.146145       0.000000       0.000000       0.007734       0.000000
      0.000000      -0.156586       0.000001       0.000000       0.000000
                     0.438056       0.000000
      0.429482       0.000000       0.000000       0.659450       0.000000
                     0.000000       0.000000       0.119624       0.000001

  O     2.30591123     0.00000000     0.00000000     Type    O       Rank   4
     -0.404631
      0.000000       0.004180       0.000000
      0.210348       0.000000       0.000000       0.075222       0.000000
      0.000000       0.365213       0.000000       0.000000       0.000000
                     0.646182       0.000000
      0.031236       0.000000       0.000000      -0.105604       0.000000
                     0.000000       0.000000      -0.233331       0.000000

 H1    -1.10295133     1.79513191     0.00000000     Type   H1       Rank   4
      0.033732
      0.000000      -0.023159       0.068068
      0.022462       0.000000       0.000000       0.028978       0.068338
      0.000000       0.124547      -0.195065       0.000000       0.000000
                     0.127340       0.009955
     -0.202324       0.000000       0.000000      -0.079883      -0.145320
                     0.000000       0.000000       0.047042      -0.086824

 H2    -1.10295133    -1.79513191     0.00000000     Type   H2       Rank   4
      0.033733
      0.000000      -0.023159      -0.068068
      0.022462       0.000000       0.000000       0.028978      -0.068338
      0.000000       0.124547       0.195065       0.000000       0.000000
                     0.127340      -0.009954
     -0.202324       0.000000       0.000000      -0.079883       0.145320
                     0.000000       0.000000       0.047042       0.086824
```

3. Benzene

```
! Multipole moments for benzene.  IP 0.3397 a.u.
! Based on DF-type : ISA

  C1     2.64623243     0.00000000     0.00000000     Type    C      Rank   4
      -0.105021
       0.000000      -0.059572      -0.000002
      -0.115783       0.000000       0.000000       0.150763      -0.000012
       0.000001      -0.250866      -0.000050       0.000000       0.000001
                      0.449358       0.000004
      -1.537576       0.000000      -0.000001      -0.052432      -0.000028
                      0.000000       0.000000       0.678563      -0.000005

  C2     1.32311622     2.29170451     0.00000000     Type    C      Rank   4
      -0.105606
       0.000000      -0.030106      -0.051758
      -0.116036       0.000000       0.000000      -0.075145       0.130550
       0.000001      -0.124077      -0.212361       0.000001       0.000001
                     -0.450408      -0.005290
      -1.538160       0.000000       0.000001       0.026459      -0.036711
                     -0.000001       0.000000      -0.341877      -0.592147

  C3    -1.32311622     2.29170451     0.00000000     Type    C      Rank   4
      -0.105623
       0.000000       0.030093      -0.051750
      -0.116011       0.000000       0.000000      -0.075117      -0.130570
       0.000000       0.123896      -0.212319       0.000000       0.000000
                      0.450401      -0.005315
      -1.538148       0.000000       0.000000       0.026526       0.036642
                      0.000000       0.000000      -0.341884       0.592152

  C4    -2.64623243     0.00000000     0.00000000     Type    C      Rank   4
      -0.105027
       0.000000       0.059559      -0.000002
      -0.115723       0.000000       0.000000       0.150794       0.000007
       0.000000       0.250943      -0.000035       0.000000       0.000000
                     -0.449133       0.000015
      -1.537478       0.000000       0.000000      -0.052420       0.000012
                      0.000000       0.000000       0.678495       0.000002

  C5    -1.32311622    -2.29170451     0.00000000     Type    C      Rank   4
      -0.105626
       0.000000       0.030092       0.051743
      -0.115985       0.000000       0.000000      -0.075133       0.130574
       0.000000       0.123942       0.212306       0.000000       0.000000
                      0.450312       0.005309
      -1.538123       0.000000       0.000000       0.026497      -0.036652
                      0.000000       0.000000      -0.341868      -0.592128

  C6     1.32311622    -2.29170451     0.00000000     Type    C      Rank   4
      -0.105617
       0.000000      -0.030103       0.051750
      -0.116009       0.000000       0.000000      -0.075155      -0.130555
       0.000000      -0.124092       0.212315       0.000000      -0.000001
                     -0.450334       0.005272
      -1.538120       0.000000       0.000000       0.026449       0.036716
                      0.000000       0.000000      -0.341879       0.592146
```

```
H1     4.70829954     0.00000000     0.00000000     Type     H      Rank   4
     0.105251
     0.000000       0.056861       0.000000
    -0.027990       0.000000       0.000000      -0.078141       0.000000
     0.000000      -0.225733       0.000002       0.000000       0.000000
                    0.034490       0.000000
    -0.209280       0.000000       0.000000       0.196346       0.000000
                    0.000000       0.000000       0.042825       0.000002

H2     2.35414977     4.07750701     0.00000000     Type     H      Rank   4
     0.105505
     0.000000       0.028469       0.049273
    -0.028002       0.000000       0.000000       0.039346      -0.067556
     0.000000      -0.113308      -0.195799       0.000000       0.000000
                   -0.035006       0.000043
    -0.209654       0.000000       0.000000      -0.098283       0.170682
                    0.000000       0.000000      -0.020876      -0.036303

H3    -2.35414977     4.07750701     0.00000000     Type     H      Rank   4
     0.105504
     0.000000      -0.028474       0.049279
    -0.028005       0.000000       0.000000       0.039346       0.067557
     0.000000       0.113310      -0.195794       0.000000       0.000000
                    0.035001       0.000045
    -0.209656       0.000000       0.000000      -0.098285      -0.170685
                    0.000000       0.000000      -0.020867       0.036302

H4    -4.70829954     0.00000000     0.00000000     Type     H      Rank   4
     0.105253
     0.000000      -0.056865       0.000000
    -0.027985       0.000000       0.000000      -0.078144       0.000000
     0.000000       0.225730       0.000000       0.000000       0.000000
                   -0.034491      -0.000001
    -0.209282       0.000000       0.000000       0.196346       0.000000
                    0.000000       0.000000       0.042818      -0.000001

H5    -2.35414977    -4.07750701     0.00000000     Type     H      Rank   4
     0.105504
     0.000000      -0.028475      -0.049282
    -0.028004       0.000000       0.000000       0.039347      -0.067558
     0.000000       0.113307       0.195793       0.000000       0.000000
                    0.035001      -0.000045
    -0.209656       0.000000       0.000000      -0.098286       0.170686
                    0.000000       0.000000      -0.020867      -0.036298

H6     2.35414977    -4.07750701     0.00000000     Type     H      Rank   4
     0.105506
     0.000000       0.028471      -0.049276
    -0.028001       0.000000       0.000000       0.039346       0.067557
     0.000000      -0.113307       0.195797       0.000000       0.000000
                   -0.035004      -0.000043
    -0.209655       0.000000       0.000000      -0.098283      -0.170682
                    0.000000       0.000000      -0.020875       0.036300
```

4. Formamide

```
! Multipole moments for formamide. IP 0.3745 a.u.
! Based on DF-type : ISA

  C     0.73690219    -0.29016270     0.00000000     Type    C       Rank    4
      0.643558
      0.000000      -0.093062       0.038727
     -0.067960       0.000000       0.000000      -0.137494      -0.106254
      0.000000      -0.017016      -0.484918       0.000000      -0.000001
                     1.387651      -0.272810
     -0.075305       0.000000       0.000002       0.131492       0.080812
                     0.000000       0.000000       0.081890      -1.175362

  O    -0.41965533    -2.26421099     0.00000000     Type    O       Rank    4
     -0.565593
      0.000000      -0.035721      -0.020417
      0.078619       0.000000       0.000000      -0.121810      -0.031359
      0.000000      -0.161251      -0.129524       0.000000       0.000000
                     0.639035      -0.240432
      0.013317       0.000000       0.000000       0.044043      -0.078437
                     0.000000       0.000000       0.251191       0.201007

  N    -0.33761508     2.03824113     0.00000000     Type    N       Rank    4
     -0.824931
      0.000000      -0.013814      -0.062137
     -0.264854       0.000000       0.000000      -0.005416       0.097960
     -0.000001       0.109101      -1.056705       0.000000       0.000000
                     1.349783      -0.459433
     -0.483980       0.000000       0.000000      -0.531023      -0.527108
                     0.000001       0.000000       0.299321       0.140845

 H1     2.82092994    -0.20596490     0.00000000     Type   H1       Rank    4
     -0.001641
      0.000000       0.077541      -0.007031
     -0.001861       0.000000       0.000000      -0.098989      -0.046376
      0.000000      -0.209632      -0.012407       0.000000       0.000000
                     0.150328       0.034063
     -0.170607       0.000000       0.000000       0.150705      -0.025453
                     0.000000       0.000000      -0.075252       0.014589

 H2    -2.23332780     2.19617606     0.00000000     Type   H2       Rank    4
      0.382741
      0.000000      -0.028215      -0.006547
      0.015378       0.000000       0.000000      -0.024566      -0.007460
      0.000000       0.165599      -0.086495       0.000000       0.000000
                    -0.116501       0.028620
     -0.161643       0.000000       0.000000       0.061183      -0.093391
                     0.000000       0.000000       0.002485      -0.005154

 H3     0.72278745     3.61139057     0.00000000     Type   H3       Rank    4
      0.365865
      0.000000       0.027500       0.013469
      0.018155       0.000000       0.000000       0.014052       0.006261
      0.000000      -0.067393      -0.158104       0.000000       0.000000
                    -0.098466       0.029778
     -0.143143       0.000000       0.000000      -0.075905       0.104982
                     0.000000       0.000000       0.016422      -0.002377
```

5. Methane

```
! Multipole moments for CH4.  IP 0.4634 a.u.
! Based on DF-type : ISA

  C     0.00000000     0.00000000     0.00000000     Type    C      Rank   4
     -0.408856
     -0.000202      -0.000002      -0.000377
      0.000484       0.000001      -0.000088       0.000685      -0.000001
      0.104779       0.000001       0.088809      -0.082229      -0.000009
                     0.000004       0.116277
      0.185492      -0.000001       0.541383       0.277448       0.000000
                     0.000000      -0.614966       0.362808      -0.000001

 H1     0.00000000     2.07703578     0.00000000     Type    H      Rank   4
      0.102417
     -0.000061       0.000000       0.032680
      0.008683       0.000000       0.000019       0.015003       0.000000
      0.053924       0.000000      -0.106577      -0.041788       0.000000
                     0.000000      -0.137930
     -0.082778       0.000000      -0.007186      -0.124064       0.000000
                     0.000000       0.008499      -0.164256       0.000000

 H2     1.69589261    -0.69234525     0.97912406     Type    H      Rank   4
      0.102242
      0.015402       0.026780      -0.010907
      0.002756      -0.011373       0.004695      -0.008331       0.008084
     -0.057979       0.014050       0.041069       0.085522      -0.124501
                     0.054163      -0.064681
      0.050136       0.095833      -0.046389      -0.041190       0.036058
                    -0.058609       0.143130      -0.006748       0.097550

 H3    -1.69589261    -0.69234525     0.97912406     Type    H      Rank   4
      0.102240
      0.015403      -0.026782      -0.010908
      0.002755       0.011372       0.004695      -0.008330      -0.008083
     -0.057979      -0.014050       0.041069       0.085522       0.124501
                    -0.054163      -0.064681
      0.050135      -0.095833      -0.046389      -0.041190      -0.036058
                     0.058608       0.143130      -0.006748      -0.097549

 H4     0.00000000    -0.69234525    -1.95824810     Type    H      Rank   4
      0.101957
     -0.031109       0.000000      -0.011077
     -0.013928       0.000000      -0.009349       0.001323       0.000000
     -0.115731       0.000000      -0.129307       0.008402       0.000000
                     0.000000       0.067636
     -0.110065       0.000000      -0.180647       0.066106       0.000000
                     0.000000       0.024363      -0.007363       0.000000
```

6. CCl_4

```
! Multipole moments for CCl4.  IP 0.423 a.u.
! Based on DF-type : ISA

  C     0.00000000     0.00000000     0.00000000   Type C   Rank 4
    0.51398
    0.00032  -0.00092   0.00094
    0.00747  -0.00383   0.00337   0.00090   0.00238
    0.00304   0.02445  -0.00721  -0.01649   1.96366
             -0.03436  -0.04071
    1.29156   0.05354  -0.03853   0.00051   0.01329
              0.02177   0.01735   1.10520  -0.01098

 Cl1    1.94458210    -1.94458210    -1.94458210   Type Cl  Rank 4
   -0.12865
    0.08914   0.08930  -0.08938
   -0.00239   0.53064  -0.52982  -0.00000  -0.53072
   -0.44180   0.27762  -0.27952   0.00210  -1.50842
             -0.35060  -0.35056
    0.13102   0.16918  -0.16750  -0.00001   0.48488
              0.45598   0.45712   0.11417  -0.00093

 Cl2   -1.94458210     1.94458210    -1.94458210   Type Cl  Rank 4
   -0.12839
    0.08718  -0.08808   0.08786
    0.00018  -0.53970   0.53904  -0.00062  -0.53965
   -0.43333  -0.26155   0.25896   0.00272  -1.46048
              0.33935   0.34445
    0.14650  -0.16238   0.16107  -0.00070   0.48291
             -0.44887  -0.44876   0.12732  -0.00091

 Cl3   -1.94458210    -1.94458210     1.94458210   Type Cl  Rank 4
   -0.12851
   -0.08815   0.08852   0.08853
   -0.00056  -0.53369  -0.53738   0.00241   0.53482
    0.43033   0.28552   0.24718  -0.00259  -1.47726
             -0.35525   0.34491
    0.14235  -0.17148  -0.16283   0.00671  -0.48092
             -0.45003   0.45160   0.11988  -0.00228

 Cl4    1.94458210     1.94458210     1.94458210   Type Cl  Rank 4
   -0.12843
   -0.08833  -0.08804  -0.08834
   -0.00119   0.53770   0.53490  -0.00245   0.53567
    0.42994  -0.25524  -0.28650   0.01171  -1.47391
              0.34065  -0.35304
    0.14057   0.16854   0.17046  -0.00772  -0.48038
              0.44610  -0.45418   0.11535   0.00446
```