Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Generation, contraction, and polarisation of Gaussian basis sets for atomic and molecular calculations using the generator coordinate method with polynomial discretization: atoms from Na through Cl

Amanda R. Guimarães,[a] Rugles C. Barbosa,[b] Ana Cristina Mora Tello,[a] Aldineia P. da Silva,[a] Júlia M. A. Alves,[a] Milena Palhares Maringolo[a] and Albérico B. F. da Silva[a]

[a]*Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil.*

[b]*Centro Regional de Ciências Nucleares do Centro Oeste a Nuclear – CRCN-CO, Abadia de Goiás – GO, Brazi*l

E-mail: alberico@iqsc.usp.br; amd_r_g@hotmail.com

Table of contents

SI. 1 pGCHF-4d2f1g(not contracted) basis sets for the from atoms Na through Cl

SI.1.1 Sodium

```
Na 0
s 10 1.0
    0.4898333E+06      0.1356130E-04
    0.1041943E+06      0.6557761E-04
    0.2555346E+05      0.3686659E-03
    0.7122238E+04      0.1598320E-02
    0.2223793E+04      0.6362441E-02
    0.7667142E+03      0.2037996E-01
    0.2877296E+03      0.6030559E-01
    0.1158504E+03      0.1256414E+00
    0.4933134E+02      0.2116083E+00
    0.2189833E+02      0.3108046E-01
s 7 1.0
    0.2223793E+04     0.1964785E-04
    0.7667142E+03    -0.7007662E-04
    0.2877296E+03    -0.1508232E-03
    0.1158504E+03    -0.3229497E-02
    0.4933134E+02    -0.1027686E-01
    0.2189833E+02    -0.4391296E-01
    0.9988770E+01    -0.3056416E-01
s 6 1.0
    0.2877296E+03     0.1233270E-04
    0.1158504E+03     0.1265678E-04
    0.4933134E+02     0.1980961E-03
    0.2189833E+02     0.3696557E-03
    0.9988770E+01     0.1415959E-02
    0.4615050E+01    -0.2451400E-02
s 1 1.0
    2.12889607         1.0
s 1 1.0
    0.96648798         1.0
s 1 1.0
    0.42565009         1.0
s 1 1.0
    0.17925596         1.0
s 1 1.0
    0.07115565         1.0
s 1 1.0
    0.02624281         1.0
p 7 1.0
    0.2672449E+04     0.3242000E-04
    0.6881847E+03     0.2767800E-03
    0.2097861E+03     0.1879500E-02
    0.7394347E+02     0.9112720E-02
```

```
    0.2943398E+02     0.3229470E-01
    0.1292408E+02     0.8668710E-01
    0.6114012E+01     0.1723980E+00
p 1 1.0
    3.04371808        1.0
p 1 1.0
    1.55743131        1.0
p 1 1.0
    0.80004565        1.0
p 1 1.0
    0.40299258        1.0
p 1 1.0
    0.19441546        1.0
p 1 1.0
    0.08773866        1.0
d 1 1.0
    1.09182426        1.0
d 1 1.0
    0.714188392       1.0
d 1 1.0
    0.584730897       1.0
d 1 1.0
    0.193148896       1.0
f 1 1.0
    0.583846756       1.0
f 1 1.0
    0.087738660       1.0
g 1 1.0
   0.265625           1.0
****
```

SI.1.2 Magnesium

```
Mg 0
 s 10 1.0
   0.6227681E+06      0.1270514E-04
   0.1360048E+06      0.5854047E-04
   0.3395530E+05      0.3198732E-03
   0.9564278E+04      0.1369970E-02
   0.2999530E+04      0.5435426E-02
   0.1033656E+04      0.1763493E-01
   0.3862654E+03      0.5289224E-01
   0.1544714E+03      0.1151851E+00
   0.6524214E+02      0.2007149E+00
   0.2872046E+02      0.6591023E-01
s 7 1.0
   0.2999530E+04       0.1585334E-04
   0.1033656E+04      -0.6597863E-04
   0.3862654E+03      -0.1796865E-03
   0.1544714E+03      -0.3131163E-02
   0.6524214E+02      -0.1111602E-01
   0.2872046E+02      -0.4603704E-01
```

```
   0.1300479E+02     -0.4090610E-01
s 4 1.0
   0.6524214E+02     0.1237367E-03
   0.2872046E+02     0.2310344E-03
   0.1300479E+02     0.1346105E-02
   0.5977626E+01    -0.1908151E-02
s 1 1.0
   2.75253886        1.0
s 1 1.0
   1.25309123        1.0
s 1 1.0
   0.55659818        1.0
s 1 1.0
   0.23805432        1.0
s 1 1.0
   0.09674998        1.0
s 1 1.0
   0.03687497        1.0
p 7 1.0
   0.4861677E+04     0.1636000E-04
   0.1298184E+04     0.1295900E-03
   0.4107481E+03     0.8388900E-03
   0.1503329E+03     0.3986090E-02
   0.6213288E+02     0.1439740E-01
   0.2830920E+02     0.4062294E-01
   0.1388104E+02     0.9328451E-01
p 1 1.0
   7.15080431        1.0
p 1 1.0
   3.77811916        1.0
p 1 1.0
   1.99863818        1.0
p 1 1.0
   1.03342807        1.0
p 1 1.0
   0.50987492        1.0
p 1 1.0
   0.23433337        1.0
d 1 1.0
  0.931646755        1.0
d 1 1.0
  0.419053857        1.0
d 1 1.0
  0.281076610        1.0
d 1 1.0
  0.0943541977       1.0
f 1 1.0
  0.333840821        1.0
f 1 1.0
  0.134186367        1.0
g 1 1.0
```

```
  0.017484018        1.0
****
```

SI.1.3 Aluminium

```
Al 0
s 10 1.0
   0.2545875E+07     0.2002485E-05
   0.4101530E+06     0.2150549E-04
   0.7993728E+05     0.1536086E-03
   0.1850382E+05     0.8417600E-03
   0.4994549E+04     0.3884870E-02
   0.1543361E+04     0.1445681E-01
   0.5360306E+03     0.4581785E-01
   0.2054358E+03     0.1083070E+00
   0.8529850E+02     0.1908434E+00
   0.3767030E+02     0.1108153E+00
s 6 1.0
   0.1543361E+04    -0.4105745E-04
   0.5360306E+03    -0.2836314E-03
   0.2054358E+03    -0.2635687E-02
   0.8529850E+02    -0.1165820E-01
   0.3767030E+02    -0.4370875E-01
   0.1737254E+02    -0.6116801E-01
s 4 1.0
   0.8529850E+02     0.9912466E-04
   0.3767030E+02     0.2277114E-03
   0.1737254E+02     0.1477573E-02
   0.8213878E+01    -0.9864054E-03
s 1 1.0
   3.90901748        1.0
s 1 1.0
   1.83838085        1.0
s 1 1.0
   0.83881437        1.0
s 1 1.0
   0.36456311        1.0
s 1 1.0
   0.14817333        1.0
s 1 1.0
   0.05529321        1.0
p 6 1.0
   0.2221656E+04     0.1034234E-03
   0.4791056E+03     0.1303645E-02
   0.1333547E+03     0.8203756E-02
   0.4592131E+02     0.3594942E-01
   0.1875234E+02     0.6744974E-01
   0.8704381E+01     0.1362460E+00
p 3 1.0
   0.1875234E+02    -0.5216766E-03
   0.8704381E+01    -0.8895048E-03
   0.4402182E+01    -0.4071342E-02
```

```
p 1 1.0
   2.32515511        1.0
p 1 1.0
   1.22940787        1.0
p 1 1.0
   0.62374401        1.0
p 1 1.0
   0.29106460        1.0
p 1 1.0
   0.11974330        1.0
p 1 1.0
   0.04162920        1.0
d 1 1.0
  3.23658096         1.0
d 1 1.0
  0.412467132        1.0
d 1 1.0
  0.144817836        1.0
d 1 1.0
  0.0288277721       1.0
f 1 1.0
  0.414916298        1.0
f 1 1.0
  0.176224365        1.0
g 1 1.0
  0.04371066         1.0
****
```

SI.1.4 Silicon

```
Si 0
s 10 1.0
  0.7143202E+06      0.1633552E-04
  0.1423194E+06      0.8705522E-04
  0.3336316E+05      0.4921341E-03
  0.9058851E+04      0.2204770E-02
  0.2804488E+04      0.8457510E-02
  0.9744958E+03      0.2629126E-01
  0.3741311E+03      0.6707160E-01
  0.1562271E+03      0.1139539E+00
  0.6984727E+02      0.9620584E-01
  0.3291351E+02     -0.1397293E+00
s 7 1.0
  0.2804488E+04     -0.4681528E-05
  0.9744958E+03     -0.1602222E-03
  0.3741311E+03     -0.1038003E-02
  0.1562271E+03     -0.6333114E-02
  0.6984727E+02     -0.2189089E-01
  0.3291351E+02     -0.5255652E-01
  0.1609171E+02     -0.2364386E-01
s 5 1.0
```

```
  0.1562271E+03     -0.1266937E-04
  0.6984727E+02      0.4175153E-04
  0.3291351E+02      0.2973784E-03
  0.1609171E+02      0.1256452E-02
  0.8035347E+01     -0.1840957E-02
s 1 1.0
  4.03416200         1.0
s 1 1.0
  2.00456238         1.0
s 1 1.0
  0.97045371         1.0
s 1 1.0
  0.45059931         1.0
s 1 1.0
  0.19753231         1.0
s 1 1.0
  0.08048021         1.0
p 6 1.0
  0.2290912E+04      0.1381968E-03
  0.5575846E+03      0.1317044E-02
  0.1663116E+03      0.8054759E-02
  0.5886081E+02      0.3249050E-01
  0.2393345E+02      0.6793096E-01
  0.1082536E+02      0.8733102E-01
p 3 1.0
  0.2393345E+02     -0.4391745E-03
  0.1082536E+02     -0.1692494E-02
  0.5273767E+01     -0.4303293E-02
p 1 1.0
   2.67931413        1.0
p 1 1.0
   1.37446446        1.0
p 1 1.0
   0.68934022        1.0
p 1 1.0
   0.32727056        1.0
p 1 1.0
   0.14240869        1.0
p 1 1.0
   0.05499273        1.0
d 1 1.0
  0.904553017        1.0
d 1 1.0
  0.621886307        1.0
d 1 1.0
  0.403477544        1.0
d 1 1.0
  0.141405216        1.0
f 1 1.0
   0.561999803       1.0
f 1 1.0
```

```
   0.198649753        1.0
g 1 1.0
  0.055563128         1.0
****
```

SI.1.5 Phosphorus

```
P 0
s 10 1.0
   0.9262659E+06     0.1272179E-04
   0.1951874E+06     0.6624560E-04
   0.4765239E+05     0.3629980E-03
   0.1328932E+05     0.1578900E-02
   0.4174210E+04     0.6128680E-02
   0.1456021E+04     0.1933267E-01
   0.5560980E+03     0.5425340E-01
   0.2292944E+03     0.1078939E+00
   0.1006381E+03     0.1615061E+00
   0.4635821E+02     0.6115892E-03
s 6 1.0
   0.1456021E+04    -0.1255638E-03
   0.5560980E+03    -0.5670197E-03
   0.2292944E+03    -0.4523457E-02
   0.1006381E+03    -0.1599564E-01
   0.4635821E+02    -0.5380219E-01
   0.2209807E+02    -0.4942879E-01
s 5 1.0
   0.2292944E+03    -0.3492358E-04
   0.1006381E+03     0.2940961E-04
   0.4635821E+02     0.2555523E-04
   0.2209807E+02     0.1520548E-02
   0.1074766E+02    -0.1232743E-02
s 1 1.0
   5.25864625         1.0
s 1 1.0
   2.55212797         1.0
s 1 1.0
   1.21134504         1.0
s 1 1.0
   0.55441958         1.0
s 1 1.0
   0.24125863         1.0
s 1 1.0
   0.09841677         1.0
p 6 1.0
   0.3736314E+04     0.6939740E-04
   0.9612032E+03     0.5972235E-03
   0.2917867E+03     0.3873090E-02
   0.1019277E+03     0.1748461E-01
   0.3995711E+02     0.4756233E-01
   0.1714228E+02     0.6420530E-01
p 4 1.0
```

```
   0.1019277E+03    -0.2171078E-04
   0.3995711E+02    -0.3245068E-03
   0.1714228E+02    -0.1809482E-02
   0.7848999E+01    -0.5070522E-02
p 1 1.0
   3.74049640        1.0
p 1 1.0
   1.80930443        1.0
p 1 1.0
   0.86628276        1.0
p 1 1.0
   0.40037918        1.0
p 1 1.0
   0.17419884        1.0
p 1 1.0
   0.06957916        1.0
d 1 1.0
   1.17119463        1.0
d 1 1.0
   0.913497416       1.0
d 1 1.0
   0.393173817       1.0
d 1 1.0
   0.148078849       1.0
f 1 1.0
   0.63482418        1.0
f 1 1.0
   0.235946343       1.0
g 1 1.0
   0.06413004        1.0
****
```

SI.1.6 Sulphur

```
S 0
 s 10 1.0
    0.1691437E+07     0.6702497E-05
    0.3489173E+06     0.3784754E-04
    0.8292252E+05     0.2218138E-03
    0.2240663E+05     0.1008950E-02
    0.6793686E+04     0.4146429E-02
    0.2281025E+04     0.1399779E-01
    0.8369917E+03     0.4294935E-01
    0.3312451E+03     0.9812530E-01
    0.1395359E+03     0.1796077E+00
    0.6174489E+02     0.9202609E-01
 s 7 1.0
    0.6793686E+04     0.3955853E-05
    0.2281025E+04    -0.5813238E-04
    0.8369917E+03    -0.3620891E-03
    0.3312451E+03    -0.3321269E-02
```

```
   0.1395359E+03    -0.1511699E-01
   0.6174489E+02    -0.5965754E-01
   0.2832474E+02    -0.9820292E-01
s 5 1.0
   0.3312451E+03    -0.8028954E-04
   0.1395359E+03    -0.2273390E-03
   0.6174489E+02    -0.1159805E-02
   0.2832474E+02    -0.4302790E-03
   0.1329386E+02    -0.7868441E-03
s 1 1.0
   6.29981264        1.0
s 1 1.0
   2.97485729        1.0
s 1 1.0
   1.38145724        1.0
s 1 1.0
   0.62260465        1.0
s 1 1.0
   0.26875817        1.0
s 1 1.0
   0.10966200        1.0
p 6 1.0
  0.4710680E+04      0.6696302E-04
  0.1014892E+04      0.7922159E-03
  0.2777730E+03      0.5740240E-02
  0.9303360E+02      0.2567171E-01
  0.3672959E+02      0.6010408E-01
  0.1646513E+02      0.7503098E-01
p 4 1.0
  0.9303360E+02     -0.4691408E-04
  0.3672959E+02     -0.6492905E-03
  0.1646513E+02     -0.2629402E-02
  0.8072970E+01     -0.6439642E-02
p 1 1.0
  4.17029844        1.0
p 1 1.0
  2.18631611        1.0
p 1 1.0
  1.12051378        1.0
p 1 1.0
  0.54078706        1.0
p 1 1.0
  0.23674818        1.0
p 1 1.0
  0.09056172        1.0
d 1 1.0
  3.16925652        1.0
d 1 1.0
  0.923015743       1.0
d 1 1.0
  0.441537301       1.0
```

```
 d 1 1.0
   0.182988886        1.0
 f 1 1.0
   0.819237322        1.0
 f 1 1.0
   0.310170358        1.0
 g 1 1.0
   0.714049587        1.0
 ****
```

SI.1.7 Chlorine

```
Cl 0
s 12 1.0
   0.5056009E+07    -0.2029651E-06
   0.1075509E+07     0.1081171E-04
   0.2613588E+06     0.6115840E-04
   0.7174829E+05     0.2719700E-03
   0.2200250E+05     0.1116961E-02
   0.7453375E+04     0.3739412E-02
   0.2757967E+04     0.1205688E-01
   0.1102339E+04     0.2859425E-01
   0.4706145E+03     0.6569682E-01
   0.2122142E+03     0.5475885E-01
   0.9994870E+02    -0.2461237E-01
   0.4861922E+02    -0.5351394E+00
s 9 1.0
   0.2200250E+05     0.1387492E-05
   0.7453375E+04    -0.5084559E-05
   0.2757967E+04     0.5827268E-06
   0.1102339E+04    -0.2586041E-03
   0.4706145E+03    -0.8879656E-03
   0.2122142E+03    -0.6132987E-02
   0.9994870E+02    -0.1635996E-01
   0.4861922E+02    -0.4513035E-01
   0.2415469E+02    -0.1142071E-01
s 6 1.0
   0.4706145E+03     0.2769529E-04
   0.2122142E+03     0.4533757E-04
   0.9994870E+02     0.4654046E-03
   0.4861922E+02     0.1149294E-02
   0.2415469E+02     0.3224297E-02
   0.1211971E+02    -0.4133925E-02
s 1 1.0
   6.07316556        1.0
s 1 1.0
   3.00541428        1.0
s 1 1.0
   1.45242812        1.0
s 1 1.0
   0.67782974        1.0
s 1 1.0
```

```
   0.30207644        1.0
s 1 1.0
   0.12712119        1.0
p 8 1.0
   0.7990193E+04     0.2943455E-04
   0.2185107E+04     0.2240571E-03
   0.6946005E+03     0.1437188E-02
   0.2516878E+03     0.6844950E-02
   0.1019464E+03     0.2396194E-01
   0.4526703E+02     0.5997733E-01
   0.2160780E+02     0.9958317E-01
   0.1087366E+02     0.1097738E+00
p 5 1.0
  0.1019464E+03     -0.6046455E-04
  0.4526703E+02     -0.5282800E-03
  0.2160780E+02     -0.2389362E-02
  0.1087366E+02     -0.5844593E-02
  0.5657112E+01     -0.1204547E-01
p 1 1.0
  2.98391211         1.0
p 1 1.0
  1.56483061         1.0
p 1 1.0
  0.80012263         1.0
p 1 1.0
  0.39117545         1.0
p 1 1.0
  0.17932067         1.0
p 1 1.0
  0.07558763         1.0
d 1 1.0
  4.95310633         1.0
d 1 1.0
  1.32077704         1.0
d 1 1.0
  0.589743149        1.0
d 1 1.0
  0.238081911        1.0
f 1 1.0
  1.05772972         1.0
f 1 1.0
  0.416529867        1.0
g 1 1.0
  0.8263684          1.0
****
```

SI. 2 Polarisation Exponents

Table SI. 2 Polarisation exponents optimised via CISD. The second d exponents (the first for the Mg atom) of the pGCHF-3d2f+d sets were "pinched" from the p uncontracted set of exponents.

pGCHF-2d1f						
Na	Mg	Al	Si	P	S	Cl
d 1 1.0 1.09182426 1.0 d 1 1.0 0.584730897 1.0 f 1 1.0 0.19441546 1.0	d 1 1.0 0.931646755 1.0 d 1 1.0 0.28107661 1.0 f 1 1.0 0.333840821. 1.0	d 1 1.0 0.327147582 1.0 d 1 1.0 0.111433639 1.0 f 1 1.0 0.254517453 1.0	d 1 1.0 0.477131273 1.0 d 1 1.0 0.161418218. 1.0 f 1 1.0 0.344193839 1.0	d 1 1.0 0.635440915 1.0 d 1 1.0 0.215883232 1.0 f 1 1.0 0.452768845 1.0	d 1 1.0 0.764482627. 1.0 d 1 1.0 0.266239039 1.0 f 1 1.0 0.571207012 1.0	d 1 1.0 1.012950600 1.0 d 1 1.0 0.336078867 1.0 f 1 1.0 0.704487390 1.0
pGCHF-3d2f						
Na	Mg	Al	Si	P	S	Cl
d 1 1.0 1.09182426 1.0 d 1 1.0 0.584730897 1.0 d 1 1.0 0.193148896 1.0 f 1 1.0 0.583846756 1.0 f 1 1.0 0.08773866 1.0	d 1 1.0 0.931646755 1.0 d 1 1.0 0.28107661 1.0 d 1 1.0 0.0943541977 1.0 f 1 1.0 0.333840821 1.0 f 1 1.0 0.134186367 1.0	d 1 1.0 0.889078903 1.0 d 1 1.0 0.281006741 1.0 d 1 1.0 0.101717936 1.0 f 1 1.0 0.414916298 1.0 f 1 1.0 0.176224365 1.0	d 1 1.0 0.97964414 1.0 d 1 1.0 0.297807679 1.0 d 1 1.0 0.107868274 1.0 f 1 1.0 0.561999803 1.0 f 1 1.0 0.198649753 1.0	d 1 1.0 1.17119463 1.0 d 1 1.0 0.393173817 1.0 d 1 1.0 0.148078849 1.0 f 1 1.0 0.63482418 1.0 f 1 1.0 0.235946343 1.0	d 1 1.0 1.64734169 1.0 d 1 1.0 0.556157655 1.0 d 1 1.0 0.208533285 1.0 f 1 1.0 0.819237322 1.0 f 1 1.0 0.310170358 1.0	d 1 1.0 1.84249742 1.0 d 1 1.0 0.667733983 1.0 d 1 1.0 0.254606906 1.0 f 1 1.0 1.05772972 1.0 f 1 1.0 0.416529867 1.0
pGCHF-3d2f+d						
Na	Mg	Al	Si	P	S	Cl
d 1 1.0 1.09182426 1.0 d 1 1.0 0.80004565 1.0 d 1 1.0 0.584730897 1.0 d 1 1.0 0.193148896 1.0 f 1 1.0 0.583846756 1.0 f 1 1.0 0.08773866 1.0	d 1 1.0 1.99863818 1.0 d 1 1.0 0.931646755 1.0 d 1 1.0 0.28107661 1.0 d 1 1.0 0.0943541977 1.0 f 1 1.0 0.333840821 1.0 f 1 1.0 0.134186367 1.0	d 1 1.0 0.889078903 1.0 d 1 1.0 0.62374401. 1.0 d 1 1.0 0.281006741 1.0 d 1 1.0 0.101717936 1.0 f 1 1.0 0.414916298 1.0 f 1 1.0 0.176224365 1.0	d 1 1.0 0.97964414 1.0 d 1 1.0 0.68934022 1.0 d 1 1.0 0.297807679 1.0 d 1 1.0 0.107868274 1.0 f 1 1.0 0.561999803 1.0 f 1 1.0 0.198649753 1.0	d 1 1.0 1.17119463 1.0 d 1 1.0 0.86628276 1.0 d 1 1.0 0.393173817 1.0 d 1 1.0 0.148078849 1.0 f 1 1.0 0.63482418 1.0 f 1 1.0 0.235946343 1.0	d 1 1.0 1.64734169 1.0 d 1 1.0 1.12051378 1.0 d 1 1.0 0.556157655 1.0 d 1 1.0 0.208533285 1.0 f 1 1.0 0.819237322 1.0 f 1 1.0 0.310170358 1.0	d 1 1.0 1.84249742 1.0 d 1 1.0 0.80012263 1.0 d 1 1.0 0.667733983 1.0 d 1 1.0 0.254606906 1.0 f 1 1.0 1.05772972 1.0 f 1 1.0 0.416529867 1.0
pGCHF-4d2f						
Na	Mg	Al	Si	P	S	Cl
d 1 1.0 1.09182426 1.0 d 1 1.0 0.714188392 1.0 d 1 1.0 0.584730897 1.0 d 1 1.0 0.193148896 1.0 f 1 1.0 0.583846756 1.0 f 1 1.0 0.08773866 1.0	d 1 1.0 0.931646755 1.0 d 1 1.0 0.419053857 1.0 d 1 1.0 0.28107661 1.0 d 1 1.0 0.0943541977 1.0 f 1 1.0 0.333840821 1.0 f 1 1.0 0.134186367 1.0	d 1 1.0 3.23658096 1.0 d 1 1.0 0.412467132 1.0 d 1 1.0 0.144817836 1.0 d 1 1.0 0.0288277721 1.0 f 1 1.0 0.414916298 1.0 f 1 1.0 0.176224365 1.0	d 1 1.0 0.904553017 1.0 d 1 1.0 0.621886307 1.0 d 1 1.0 0.403477544 1.0 d 1 1.0 0.141405216 1.0 f 1 1. 0 0.561999803 1.0 f 1 1.0 0.198649753 1.0	d 1 1.0 1.17119463 1.0 d 1 1.0 0.913497416 1.0 d 1 1.0 0.393173817 1.0 d 1 1.0 0.148078849 1.0 f 1 1.0 0.63482418 1.0 f 1 1.0 0.235946343 1.0	d 1 1.0 3.16925652 1.0 d 1 1.0 0.923015743 1.0 d 1 1.0 0.441537301 1.0 d 1 1.0 0.182988886 1.0 f 1 1.0 0.819237322 1.0 f 1 1.0 0.310170358 1.0	d 1 1.0 4.95310633 1.0 d 1 1.0 1.32077704 1.0 d 1 1.0 0.589743149 1.0 d 1 1.0 0.238081911 1.0 f 1 1.0 1.05772972. 1.0 f 1 1.0 0.416529867 1.0
pGCHF-4d2f1g(contracted)						
Na	Mg	Al	Si	P	S	Cl
d 1 1.0 1.09182426 1.0 d 2 1.0 0.714188392 0.1868 0.584730897 0.8132 d 1 1.0 0.193148896 1.0 f 2 1.0 0.583846756 0.169 0.08773866 0.8310 g 1 1.0 0.265625 1.0	d 1 1.0 0.931646755 1.0 d 2 1.0 0.419053857 0.8629 0.28107661 0.1371 d 1 1.0 0.0943541977 1.0 f 2 1.0 0.333840821 0.1695 0.134186367 0.8305 g 1 1.0 0.017484018 1.0	d 1 1.0 3.23658096 1.0 d 2 1.0 0.412467132 0.3903 0.144817836 0.6097 d 1 1.0 0.0288277721 1.0 f 2 1.0 0.414916298 0.4479 0.176224365 0.5521 g 1 1.0 0.04371066 1.0	d 1 1.0 0.904553017 1.0 d 2 1.0 0.621886307 0.8648 0.403477544 0.1352 d 1 1.0 0.141405216 1.0 f 2 1.0 0.561999803 0.3550 0.198649753. 0.6450 g 1 1.0 0.055563128 1.0	d 1 1.0 1.17119463 1.0 d 2 1.0 0.913497416 0.6429 0.393173817 0.3571 d 1 1.0 0.148078849 1.0 f 2 1.0 0.63482418 0.1400 0.235946343 0.8600 g 1 1.0 0.06413004 1.0	d 1 1.0 3.16925652 1.0 d 2 1.0 0.923015743 0.3427 0.441537301 0.6573 d 1 1.0 0.182988886 1.0 f 2 1.0 0.81923732 0.1203 0.310170358 0.8797 g 1 1.0 0.714049587 1.0	d 1 1.0 4.95310633 1.0 d 2 1.0 1.32077704 0.4963 0.589743149 0.5037 d 1 1.0 0.238081911 1.0 f 2 1.0 1.05772972 0.1555 0.416529867 0.8445 g 1 1.0 0.8263684 1.0

SI. 3 Geometries, Charge and Multiplicity

System	Charge	Multiplicity	Geometry			
Cl	0	2	Cl	0.00000000	0.00000000	0.00000000
Al	0	2	Al	0.00000000	0.00000000	0.00000000
S	0	3	S	0.00000000	0.00000000	0.00000000
P	0	4	P	0.00000000	0.00000000	0.00000000
Si	0	3	Si	0.00000000	0.00000000	0.00000000
Mg	0	1	Mg	0.00000000	0.00000000	0.00000000
Na	0	2	Na	0.00000000	0.00000000	0.00000000
Al2	0	3	Al	0.00000000	0.00000000	1.42325100
			Al	0.00000000	0.00000000	-1.42325100
AlCl	0	1	Al	0.00000000	0.00000000	-1.30115800
			Cl	0.00000000	0.00000000	0.99500400
$AlCl_3$	0	1	Al	0.00000000	0.00000000	0.00000000
			Cl	0.00000000	2.15116400	0.00000000
			Cl	1.86296300	-1.07558200	0.00000000
			Cl	-1.86296300	-1.07558200	0.00000000
AlP	0	3	Al	0.00000000	0.00000000	-1.14990300
			P	0.00000000	0.00000000	0.99658300
AlS	0	2	Al	0.00000000	0.00000000	-1.17330800
			S	0.00000000	0.00000000	0.95331300
PCl	0	3	P	2.86600000	0.00000000	0.00000000
			Cl	4.61333048	1.00873483	0.00000000
Cl2	0	1	Cl	0.00000000	0.00000000	0.00000000
			Cl	0.00000000	0.00000000	1.98790000
Mg_2	0	1	Mg	0.00000000	0.00000000	0.00000000
			Mg	0.00000000	0.00000000	3.89050000
MgCl	0	2	Mg	0.00000000	0.00000000	-1.34960200
			Cl	0.00000000	0.00000000	0.95266000
$MgCl_2$	0	1	Mg	0.00000000	0.00000000	0.00000000
			Cl	0.00000000	0.00000000	2.24053900
			Cl	0.00000000	0.00000000	-2.24053900

Table SI. 3 (cont.)

System	Charge	Multiplicity	Geometry			
MgS	0	1	Mg	0.00000000	0.0000000	-1.26491800
			S	0.00000000	0.0000000	0.94868800
NaCl	0	1	Na	2.00000000	0.00000000	0.00000000
			Cl	4.36080000	0.00000000	0.00000000
P_2	0	1	P	0.00000000	0.00000000	0.00000000
			P	0.00000000	0.00000000	1.89340000
P_4	0	1	P	0.83894500	0.83894500	0.83894500
			P	-0.83894500	-0.83894500	0.83894500
			P	0.83894500	-0.83894500	-0.83894500
			P	-0.83894500	0.83894500	-0.83894500
PCl_3	0	1	P	0.00000000	0.00000000	0.80166700
			Cl	0.00000000	1.99886800	-0.23578500
			Cl	1.73107000	-0.99943400	-0.23578500
			Cl	-1.73107000	-0.99943400	-0.23578500
PCl_5	0	1	P	0.00000000	-0.00000000	0.00000000
			Cl	0.00000000	2.05073117	0.00000000
			Cl	1.77598529	-1.02536558	0.00000000
			Cl	0.00000000	-0.00000000	2.16025500
			Cl	-1.77598529	-1.02536559	0.00000000
			Cl	-0.00000000	-0.0000000	-2.160255000
S_2	0	3	S	0.00000000	0.00000000	0.00000000
			S	0.00000000	0.00000000	1.88920000
S_2Cl_2	0	1	S	0.50893600	0.94758900	0.80695200
			S	-0.50893600	-0.94758900	0.80695200
			Cl	-0.50893600	2.25720600	-0.75948400
			Cl	0.50893600	-2.25720600	-0.75948400
S_3	0	1	S	0.00000000	0.00000000	0.75304300
			S	0.00000000	1.79089500	-0.37652100
			S	0.00000000	-1.79089500	-0.37652100
SCl	0	2	S	0.00000000	0.00000000	-1.13260800
			Cl	0.00000000	0.00000000	1.06598400
$SiCl_2$	0	1	Si	0.00000000	0.00000000	1.00907300
			Cl	0.00000000	1.74158500	-0.41550100
			Cl	0.00000000	-1.74158500	-0.41550100
SCl_2	0	1	S	0.00000000	0.00000000	0.94220120
			Cl	0.00000000	1.75094300	-0.44338880
			Cl	0.00000000	-1.75094300	-0.44338880
Si_2	0	3	Si	0.00000000	0.00000000	0.00000000
			Si	0.00000000	0.00000000	2.24600000

Table SI. 3 (cont.)

System	Charge	Multiplicity	Geometry			
SiCl	0	2	Si	0.00000000	0.00000000	1.09677419
			Cl	0.00000000	0.00000000	-0.90322581
SiP	0	2	Si	0.54701847	0.73426572	0.00000000
			P	-1.53048153	0.73426572	0.00000000
SiS	0	1	Si	-0.00000000	-0.00000000	-1.02896000
			S	-0.00000000	-0.00000000	0.90034000

SI. 4 Total Energies

Table SI. 4 - Total energies calculated using the M062X exchange–correlation functional with the pGCHF, pcseg-3, Sapporo-QZP, and def2-QZVP basis sets.

		pGCHF 3d2f+d		pGCHF 4d2f		pGCHF 3d2f1g		pGCHF 4d2f1g (not contracted)		pGCHF 4d2f1g (contracted)		pcseg-3		def2-QZVP		Sapporo-QZP	
Molecules	symmetry	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)
										(Eh)							
Al_2	$D_{\infty h}$	-484.75736	48.1	-484.75724	48.7	-484.75716	104.3	-484.75727	97.8	-484.75664	90.9	-484.75542	67.4	-484.75623	85.8	-484.73614	78.7
AlCl	$C_{\infty v}$	-702.69517	82.9	-702.69540	82.5	-702.69514	138.7	-702.69545	168.9	-702.69521	121.3	-702.69430	108.6	-702.69529	124.8	-702.66864	130.5
$AlCl_3$	D_{3h}	-1623.28745	174.3	-1623.28850	172.4	-1623.28745	279.1	-1623.28870	331.9	-1623.28792	226.4	-1623.28613	205.8	-1623.28898	250.5	-1623.22914	267.7
AlP	$C_{\infty v}$	-583.69340	128.5	-583.69342	131.6	-583.69329	215.1	-583.69344	262.5	-583.69317	174	-583.69163	174.5	-583.69212	212.4	-583.66923	191.8
AlS	$C_{\infty v}$	-640.61755	123.4	-640.61784	123	-640.61759	207.6	-640.61794	246.5	-640.61471	200.4	-640.61666	168.1	-640.61734	200.5	-640.59222	180.3
PCl	$C_{\infty v}$	-801.53106	113.6	-801.53146	110	-801.53102	186.3	-801.53165	221.1	-801.53072	159	-801.52977	140.8	-801.53106	164.3	-801.50153	158.3
Cl_2	$D_{\infty h}$	-920.38977	40.6	-920.39069	28.2	-920.38968	70.8	-920.39113	83.1	-920.39010	46.5	-920.38931	55.4	-920.39104	62.3	-920.35746	30.9
Na_2	$D_{\infty h}$	-324.54629	40.2	-324.546286	42.3	-324.546281	75.1	-324.54629	93.2	-324.54626	74.4	-324.54376	7.8	-324.54096	13.0	-324.53408	98.5
Mg_2	$D_{\infty h}$	-400.12651	37.7	-400.12653	39	-400.12655	63.6	-400.12658	77.1	-400.12651	61.8	-400.12658	12	-400.12211	15.1	-400.11354	93.2
MgCl	$C_{\infty v}$	-660.33081	132.7	-660.33087	136.1	-660.33055	214	-660.33090	270.5	-660.32975	185.6	-660.32979	73.1	-660.32949	105.1	-660.30886	228
$MgCl_2$	$D_{\infty h}$	-1120.65171	125.3	-1120.65191	126.4	-1120.65131	201.2	-1120.65196	248.3	-1120.65068	175.8	-1120.64877	87.6	-1120.65029	124.1	-1120.61319	239.5
MgS	$C_{\infty v}$	-598.24061	84.1	-598.24158	85.5	-598.24025	139.3	-598.24169	164.5	-598.23934	121.9	-598.24308	23.1	-598.24253	81.9	-598.22367	187.8
P_2	$D_{\infty h}$	-682.69569	41.1	-682.69569	41	-682.69562	68.6	-682.69569	82.9	-682.69495	63.4	-682.69560	62.7	-682.69586	69.6	-682.66965	77.4

Table SI 4 Total Energy (cont.)

		pGCHF 3d2f+d		pGCHF 4d2f		pGCHF 3d2f1g		pGCHF 4d2f1g (not contracted)		pGCHF 4d2f1g (contracted)		pcseg-3		def2-QZVP		Sapporo-QZP	
Molecules	symmetry	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)	Total Energy	CPU time (s)
										(Eh)							
P_4	T_d	-1365.49715	133.4	-1365.49720	133.3	-1365.496776	207.8	-1365.49724	244.1	-1365.49313	178.3	-1365.49870	171.3	-1365.49829	197.5	-1365.44582	166.4
PCl_3	C_{3V}	-1722.07246	389.8	-1722.07346	381.6	-1722.072357	611.6	-1722.07392	768.2	-1722.07092	516.2	-1722.07238	465.4	-1722.07511	559.8	-1722.01159	588
PCl_5	D_{3h}	-2642.48984	737	-2642.48920	569.1	-2642.489532	1325.1	-2642.49232	1361.5	-2642.48691	1265.5	-2642.49083	798.7	-2642.49510	1032.5	-2642.39772	1086.9
S_2	$D_{\infty h}$	-796.38175	49.6	-796.38280	50.3	-796.3820591	85.4	-796.38332	105.2	-796.38297	75	-796.38161	73.2	-796.38278	85.2	-796.35292	80.4
S_2Cl_2	C_2	-1716.83030	1234.2	-1716.83253	1191.9	-1716.830681	1952.9	-1716.83364	2597.4	-1716.83212	1728.5	-1716.83089	1438.3	-1716.83350	1827.1	-1716.76959	1890.9
S_3	C_{2v}	-1194.58029	311.7	-1194.58266	303.1	-1194.580896	513.6	-1194.58363	622.5	-1194.58304	422.9	-1194.58201	407.5	-1194.58342	503.6	-1194.53765	510
SCl	$C_{\infty v}$	-858.36547	179.8	-858.36631	176.5	-858.3655189	302.1	-858.36676	364.5	-858.36606	258.4	-858.36499	230.7	-858.36649	217.1	-858.33481	267.1
$SiCl_2$	C_{2V}	-1209.98722	263.5	-1209.98780	260.3	-1209.987284	424.1	-1209.98807	508.6	-1209.98654	357.5	-1209.98774	281.5	-1209.98954	380.8	-1209.94465	340.7
SCl_2	C_{2V}	-1318.61180	277.7	-1318.61332	271.3	-1318.611936	457.9	-1318.61408	552.2	-1318.61277	389.9	-1318.61176	342.7	-1318.61397	414.4	-1318.56526	431.7
Si_2	$D_{\infty h}$	-578.83708	60.5	-578.83719	63	-578.8369554	96.8	-578.83722	124.3	-578.83673	87.50	-578.83792	74.7	-578.83855	104.3	-578.81597	84
SiCl	$C_{\infty v}$	-749.67232	186.4	-749.67267	175.2	-749.6722852	292.1	-749.67267	174.9	-749.67197	251.1	-749.67251	177.4	-749.67360	263.6	-749.64549	199
SiP	$C_{\infty v}$	-630.74848	209.3	-630.74853	209.8	-630.7483447	316.3	-630.74854	399.8	-630.74796	266.5	-630.74889	225.6	-630.74908	338	-630.72478	240.8
SiS	$C_{\infty v}$	-687.70025	82.4	-687.70064	84	-687.7004417	137.6	-687.70086	172.4	-687.70027	122.9	-687.70135	105	-687.70181	137.4	-687.67537	113.5
Mean CPU time (s)			**203.37**		**193.7**		**334.12**		397.84		**293.14**		**229.96**		**291.18**		**306.23**

SI.5 Complete Basis Set Limit Extrapolations

The energies at CBS limit were calculated through Karton and Marting's[1] formula:

$$E_{CBS} = E_L + \frac{E_L - E_{L-1}}{\frac{E \exp\left(9\left(\sqrt{L}-\sqrt{L-1}\right)\right)}{L+1}-1} \quad \text{(SI5.1)}$$

To access the accuracy of the basis sets studied in this work energies calculated with Jensen's pcseg-3 and pcseg-4 basis sets were extrapolated by turning the Equation SI4.1 into:

$$E_{CBS_{\text{pcseg}-3/\text{pcseg}-4}} = E_4 + \frac{E_4 - E_3}{\frac{4}{5}\exp\left(9\left(\sqrt{4}-\sqrt{3}\right)\right)-1} \quad \text{(SI5.2)}$$

were $E_3$and $E_4$are the total energies calculated with the pcseg-3 and pcseg-4 uncontracted basis sets respectively, using the exchange–correlation functional M062X.

Following the same pattern previously described, we have also extrapolated energies using Dunning's cc-pVQZ and cc-pV5Z uncontracted basis set through the formula:

$$E_{CBS_{\text{cc}-\text{pVQZ}/\text{cc}-\text{pV5Z}}} = E_5 + \frac{E_5 - E_4}{\frac{5}{6}\exp\left(9\left(\sqrt{5}-\sqrt{4}\right)\right)-1} \quad \text{(SI5.3)}$$

The resultant extrapolated energies are found in Table SI5.1:

Table SI5.1- Extrapolated energies calculated according to Equations SI5.2 and SI5.3.

Molecules	$E_{CBS_{\text{pcseg}-3/\text{pcseg}-4}}$	$E_{CBS_{\text{cc}-\text{pVQZ}/\text{cc}-\text{pV5Z}}}$
Al_2	-484.7646429	-484.7613542
AlCl	-702.7024417	-702.6995137
$AlCl_3$	-1623.3026915	-1623.296794
AlP	-583.7001572	-583.6969097
AlS	-640.6248141	-640.6216988
PCl	-801.5387845	-801.5356707
Cl_2	-920.3977379	-920.3949551
Na_2	-324.5527273	-324.5513731
Mg_2	-400.1330793	-400.1319339
MgCl	-660.3386073	-660.3367233
$MgCl_2$	-1120.6623143	-1120.659066
MgS	-598.2513469	-598.2494699
P_2	-682.7027695	-682.6996399
P_4	-1365.5117890	-1365.506113
PCl_3	-1722.0884177	-1722.082869
PCl_5	-2642.5150987	-2642.506746
S_2	-796.3897424	-796.3869034
S_2Cl_2	-1716.8468845	-1716.841231
S_3	-1194.5937602	-1194.589097
SCl	-858.3732612	-858.370599
$SiCl_2$	-1209.9997938	-1209.995572
SCl_2	-1318.6240028	-1318.619835
Si_2	-578.8559424	-578.8516187
SiCl	-749.6809425	-749.6779534
SiP	-630.7565451	-630.7534103
SiS	-687.7087996	-687.7059648

SI. 6 Atomisation Energies

Table SI. 6 – Atomisation Energies calculated using the M062X exchange–correlation functional with the pGCHF, pcseg-3, Sapporo-QZP and def2-QZVP basis sets and the CBS limits.

System	pGCHF-2d1f	pGCHF-4d2f1g (contracted)	pGCHF-3d2f	pGCHF-3d2f1g	pGCHF-3d2f+d	pGCHF-4d2f	pGCHF-4d2f1g (not contracted)	Sapporo-QZP	def2-QZVP	pcseg-3	CBS (cc-pVQZ/cc-pV5Z)	CBS (pcseg-3/pcseg-4)
$Al_2 \rightarrow 2Al$	33.55	34.24	34.53	34.32	34.20	34.54	34.34	34.60	34.57	34.35	34.23	34.24
$AlCl \rightarrow Al+Cl$	122.58	123.28	123.22	123.12	123.05	123.34	123.28	123.61	123.65	123.84	123.28	123.26
$AlCl_3 \rightarrow Al+3Cl$	307.32	310.01	308.44	309.43	309.40	309.05	310.16	309.68	309.82	310.17	310.26	310.46
$AlP \rightarrow Al+P$	54.84	55.28	55.51	55.43	55.38	55.57	55.50	56.03	56.24	56.42	55.42	55.24
$AlS \rightarrow Al+S$	98.37	99.39	99.19	99.32	99.20	99.38	99.50	99.45	99.78	100.04	99.36	99.40
$PCl \rightarrow P+Cl$	80.50	81.05	81.29	81.32	81.38	81.59	81.70	82.20	82.54	82.74	82.10	82.03
$Cl_2 \rightarrow 2Cl$	58.34	59.78	59.13	59.17	59.28	59.79	60.05	59.75	60.09	60.34	60.02	60.12
$Na_2 \rightarrow 2Na$	19.97	20.01	20.01	20.02	20.02	19.99	20.02	20.06	20.22	20.05	20.02	19.81
$Mg_2 \rightarrow 2Mg$	0.51	0.72	1.22	0.75	0.72	1.23	0.76	1.54	1.58	1.53	1.32	1.24
$MgCl \rightarrow Mg+Cl$	73.50	75.23	75.56	75.41	75.60	75.68	75.62	76.63	76.54	76.31	76.65	76.61
$MgCl_2 \rightarrow Mg+2Cl$	182.79	183.77	183.96	184.00	184.31	184.16	184.39	184.70	184.59	183.90	185.02	185.01
$MgS \rightarrow Mg+S$	42.12	43.83	44.43	43.61	43.85	44.91	44.49	47.03	47.09	49.87	46.82	46.70
$P_2 \rightarrow 2P$	116.71	116.85	117.69	118.08	118.12	117.73	118.13	119.38	120.16	120.69	118.77	118.33
$P_4 \rightarrow 4P$	298.94	298.86	300.77	302.38	302.61	301.05	302.68	304.77	306.37	308.01	304.58	303.34
$PCl_3 \rightarrow P+3Cl$	233.22	234.86	234.64	235.65	235.81	235.41	236.59	236.80	237.73	238.35	237.66	237.46
$PCl_5 \rightarrow P+5Cl$	307.37	311.22	309.79	312.07	312.41	309.70	313.76	313.31	314.76	315.74	315.83	315.74
$S_2 \rightarrow 2S$	102.26	104.35	103.61	104.11	103.95	104.36	104.86	104.57	105.10	105.45	104.80	104.79
$S_2Cl_2 \rightarrow 2S+2Cl$	196.61	201.46	198.90	200.26	200.11	200.54	202.06	200.83	201.98	202.75	202.08	202.18
$S_3 \rightarrow 3S$	156.73	162.00	159.83	161.07	160.73	161.50	162.73	161.70	163.09	163.84	162.68	162.93
$SCl \rightarrow S+Cl$	67.73	69.29	68.71	68.87	68.88	69.34	69.62	69.46	69.86	70.13	69.65	69.60
$SiCl_2 \rightarrow Si+2Cl$	207.83	208.92	208.80	209.13	209.10	209.13	209.54	209.95	210.43	210.85	210.19	210.02
$SCl_2 \rightarrow S+2Cl$	128.67	131.70	135.06	130.82	130.80	131.37	132.11	131.51	132.23	132.72	132.14	132.21
$Si_2 \rightarrow 2Si$	79.93	80.15	75.07	75.13	75.12	75.13	75.19	75.99	76.25	76.29	80.94	81.32
$SiCl \rightarrow Si+Cl$	103.47	104.09	104.15	104.15	104.16	104.35	104.32	104.79	105.11	105.31	104.79	104.67
$SiP \rightarrow Si+P$	84.51	84.63	85.14	85.35	85.38	85.21	85.42	86.39	86.85	87.29	85.91	85.51
$SiS \rightarrow Si+S$	145.39	146.60	146.30	146.68	146.54	146.50	146.87	147.22	147.74	148.21	147.28	146.99
RMSD $CBS_{(cc\text{-}pVQZ/cc\text{-}pV5Z)}$	**3.30**	**1.82**	**1.46**	**1.39**	**1.32**	**1.09**	**0.84**	**1.08**	**1.32**	**1.72**		
RMSD $CBS_{(pcseg\text{-}3/pcseg\text{-}4)}$	**3.21**	**1.62**	**1.39**	**1.31**	**1.26**	**1.00**	**0.72**	**1.28**	**1.56**	**1.96**		

Reference

A. Karton, J. M. L. Martin. Theor. Chem. Acc., 2006, **115**, 330-333.