Spin-Flip Luminescence

Supporting Information

Winald Robert Kitzmann*, Johannes Moll, Katja Heinze*

Department of Chemistry, Duesbergweg 10–14, Johannes Gutenberg University Mainz, Germany

Corresponding authors: Winald Robert Kitzmann, e-mail: kitzmann@uni-mainz.de, 0000-0003-0339-2196; Prof. Dr. Katja Heinze, e-mail: Katja.Heinze@Uni-Mainz.de, 0000-0003-1483-4156

CASSCF Calculations for the Empirical Assignment of Microstates in Tanabe-Sugano Diagrams

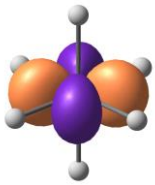
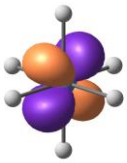
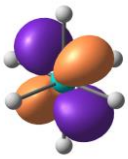
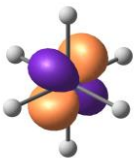
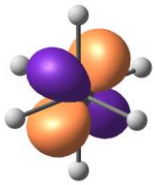
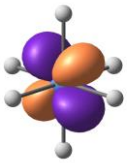
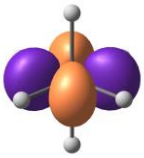
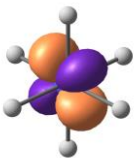
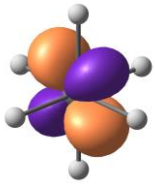
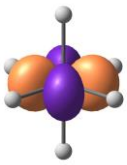
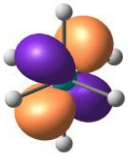
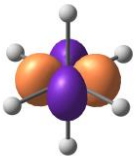
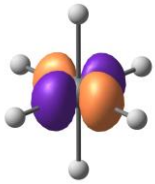
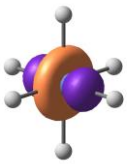
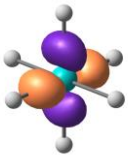
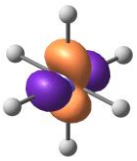
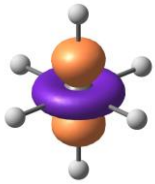
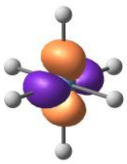
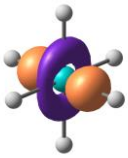
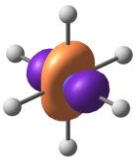
Complete Active Space Self-Consistent Field (CASSCF) calculations of perfectly octahedral hexahydrido complexes $[MH_6]^{n-}$ (M = V^{III}, Cr^{III}, Mo^{II}, Ni^{II}) with M–H bond lengths of 1.5 Å were performed. The occupation of the calculated excited metal-centered states was used for the empirical assignment of microstates in the Tanabe-Sugano diagrams (Figure 1 in main manuscript). Mo^{II} was used instead of Cr^{II} to obtain a low-spin ground state.

All calculations were performed using the quantum computing suite ORCA 5.0.2 [1]. The zeroth order relativistic approximation was used to describe relativistic effects in all calculations (keyword ZORA) [2–4]. To account for solvent effects, a conductor-like screening model (keyword CPCM acetonitrile) modeling acetonitrile was used in all calculations [5]. Explicit counter ions and/or solvent molecules were neglected.

Quasi-restricted orbitals obtained from DFT calculations (UKS) were used as an initial guess using the B3LYP functional [6] in combination with Ahlrichs' split-valence triple-zeta basis set def2-TZVPP [7] with the def2/J auxiliary basis [8] for all atoms in the 3d complexes (V, Cr, Ni) and TZVP [7] without auxiliary basis for all atoms in $[MoH_6]^{4-}$. All DFT-UKS calculations make use of the resolution of identity approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (RIJCOSX) [9,10]. Grimme's empirical dispersion correction D3BJ was employed (keyword D3BJ) [11,12].

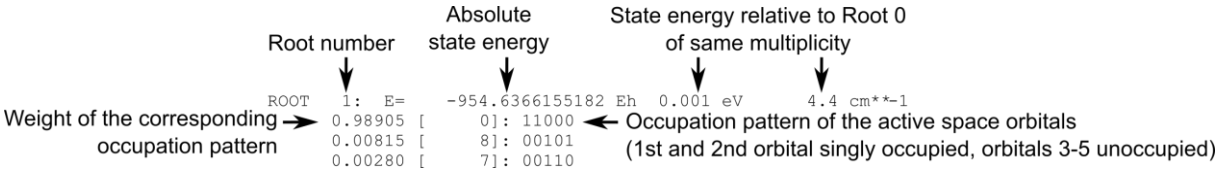
All CASSCF calculations were performed with Ahlrichs' split-valence triple-zeta basis set def2-TZVPP [7] with the def2/JK auxiliary basis [13] for all atoms in the 3d complexes (V, Cr, Ni) and TZVP with automatically generated auxiliary basis (keyword AutoAux) [14] for all atoms in $[MoH_6]^{4-}$. All calculations made use of the resolution of identity (RI-JK) approach for the Coulomb and exchange term [9,15]. The active space consisted of the 3d (V, Cr, Ni) or 4d (Mo) orbitals, respectively (see Table S1). The calculations were performed state-averaged (see Table S1 for details). The converger SuperCI was used far off convergence (keyword: orbstep SuperCI) and the converger DIIS was used close to convergence (keyword: switchstep DIIS).

Table S1: Details of the CASSCF calculations. Orbitals are shown at an isosurface value of 0.1 au.

	$[VH_6]^{4-}$ (d^2)	$[CrH_6]^{3-}$ (d^3)	$[MoH_6]^{4-}$ (d^4)	$[NiH_6]^{4-}$ (d^8)
Calculation	CAS(2,5)	CAS(3,5)	CAS(4,5)	CAS(8,5)
Multiplicities	3, 1	4, 2	5, 3, 1	3, 1
Number of Roots	10, 10	10, 10	5, 10, 10	10, 10
CAS Orbital 1				
CAS Orbital 2				
CAS Orbital 3				
CAS Orbital 4				
CAS Orbital 5				

CASSCF Results: Orbital Occupations

Legend:



d^2: Orbital Occupation in $[VH_6]^{4-}$

```
-------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 3 NROOTS=10
-------------------------------------------

ROOT   0:  E=    -954.6366355877 Eh
      0.98906 [     1]: 10100
      0.00817 [     6]: 01001
      0.00278 [     5]: 01010
ROOT   1:  E=    -954.6366155182 Eh  0.001 eV      4.4 cm**-1
      0.98905 [     0]: 11000
      0.00815 [     8]: 00101
      0.00280 [     7]: 00110
ROOT   2:  E=    -954.6359136776 Eh  0.020 eV    158.4 cm**-1
      0.98862 [     4]: 01100
      0.01138 [     2]: 10010
ROOT   3:  E=    -954.5089215469 Eh  3.475 eV  28030.0 cm**-1
      0.77288 [     5]: 01010
      0.22711 [     6]: 01001
ROOT   4:  E=    -954.5088961393 Eh  3.476 eV  28035.6 cm**-1
      0.77152 [     7]: 00110
      0.22847 [     8]: 00101
ROOT   5:  E=    -954.5084926674 Eh  3.487 eV  28124.1 cm**-1
      1.00000 [     3]: 10001
ROOT   6:  E=    -954.4769612002 Eh  4.345 eV  35044.5 cm**-1
      0.98862 [     2]: 10010
      0.01138 [     4]: 01100
ROOT   7:  E=    -954.4742884502 Eh  4.418 eV  35631.1 cm**-1
      0.76338 [     8]: 00101
      0.22568 [     7]: 00110
      0.01094 [     0]: 11000
ROOT   8:  E=    -954.4742234560 Eh  4.419 eV  35645.3 cm**-1
      0.76472 [     6]: 01001
      0.22434 [     5]: 01010
      0.01093 [     1]: 10100
ROOT   9:  E=    -954.3492417085 Eh  7.820 eV  63075.7 cm**-1
      1.00000 [     9]: 00011

-------------------------------------------
CAS-SCF STATES FOR BLOCK  2 MULT= 1 NROOTS=10
-------------------------------------------

ROOT   0:  E=    -954.5876810226 Eh
      0.99292 [     2]: 10100
      0.00533 [     7]: 01010
ROOT   1:  E=    -954.5876530320 Eh  0.001 eV      6.1 cm**-1
      0.99297 [     1]: 11000
      0.00527 [    10]: 00110
ROOT   2:  E=    -954.5870839513 Eh  0.016 eV    131.0 cm**-1
      0.99307 [     6]: 01100
      0.00693 [     4]: 10001
ROOT   3:  E=    -954.5861964386 Eh  0.040 eV    325.8 cm**-1
      0.67214 [     0]: 20000
      0.17288 [     9]: 00200
      0.15406 [     5]: 02000
ROOT   4:  E=    -954.5853835309 Eh  0.063 eV    504.2 cm**-1
      0.50862 [     5]: 02000
      0.49030 [     9]: 00200
ROOT   5:  E=    -954.5184598118 Eh  1.884 eV  15192.3 cm**-1
      0.33014 [     5]: 02000
      0.32963 [     9]: 00200
      0.32049 [     0]: 20000
      0.00995 [    12]: 00020
```

```
      0.00979 [    14]: 00002
ROOT   6:  E=    -954.4710299437 Eh  3.174 eV  25602.0 cm**-1
      0.80495 [     7]: 01010
      0.18801 [     8]: 01001
      0.00704 [     2]: 10100
ROOT   7:  E=    -954.4709731149 Eh  3.176 eV  25614.4 cm**-1
      0.80499 [    10]: 00110
      0.18802 [    11]: 00101
      0.00699 [     1]: 11000
ROOT   8:  E=    -954.4700867776 Eh  3.200 eV  25809.0 cm**-1
      0.99306 [     4]: 10001
      0.00693 [     6]: 01100
ROOT   9:  E=    -954.4603997722 Eh  3.463 eV  27935.0 cm**-1
      0.99999 [     3]: 10010
```

d^3: Orbital Occupation in $[CrH_6]^{3-}$

```
-------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 4 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -1056.7598708015 Eh
      1.00000 [     0]: 11100
ROOT   1:  E=   -1056.6237442623 Eh  3.704 eV  29876.3 cm**-1
      0.76561 [     3]: 10110
      0.23438 [     4]: 10101
ROOT   2:  E=   -1056.6237315935 Eh  3.705 eV  29879.1 cm**-1
      0.76460 [     1]: 11010
      0.23539 [     2]: 11001
ROOT   3:  E=   -1056.6225959555 Eh  3.735 eV  30128.3 cm**-1
      1.00000 [     7]: 01101
ROOT   4:  E=   -1056.5875668113 Eh  4.689 eV  37816.4 cm**-1
      0.97378 [     6]: 01110
      0.02622 [     5]: 10011
ROOT   5:  E=   -1056.5864656394 Eh  4.719 eV  38058.0 cm**-1
      0.74477 [     2]: 11001
      0.22882 [     1]: 11010
      0.02642 [     9]: 00111
ROOT   6:  E=   -1056.5864490894 Eh  4.719 eV  38061.7 cm**-1
      0.74574 [     4]: 10101
      0.22784 [     3]: 10110
      0.02642 [     8]: 01011
ROOT   7:  E=   -1056.4528969020 Eh  8.353 eV  67373.0 cm**-1
      0.97357 [     8]: 01011
      0.01988 [     4]: 10101
      0.00655 [     3]: 10110
ROOT   8:  E=   -1056.4528892268 Eh  8.353 eV  67374.7 cm**-1
      0.97358 [     9]: 00111
      0.01985 [     2]: 11001
      0.00658 [     1]: 11010
ROOT   9:  E=   -1056.4528787200 Eh  8.354 eV  67377.0 cm**-1
      0.97378 [     5]: 10011
      0.02622 [     6]: 01110

-------------------------------------------
CAS-SCF STATES FOR BLOCK  2 MULT= 2 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -1056.6792845418 Eh
      0.98060 [     5]: 11100
      0.00799 [    15]: 02010
      0.00798 [    23]: 00210
ROOT   1:  E=   -1056.6792039822 Eh  0.002 eV     17.7 cm**-1
      0.98066 [     5]: 11100
      0.01217 [     3]: 20001
ROOT   2:  E=   -1056.6758698673 Eh  0.093 eV    749.4 cm**-1
      0.49429 [     8]: 10200
      0.49420 [     4]: 12000
      0.00570 [    19]: 01101
      0.00473 [    18]: 01110
ROOT   3:  E=   -1056.6758314561 Eh  0.094 eV    757.9 cm**-1
      0.49615 [    14]: 02100
      0.49230 [     1]: 20100
      0.00549 [     6]: 11010
      0.00496 [     7]: 11001
ROOT   4:  E=   -1056.6758313617 Eh  0.094 eV    757.9 cm**-1
      0.49620 [    17]: 01200
      0.49226 [     0]: 21000
      0.00549 [     9]: 10110
      0.00496 [    10]: 10101
ROOT   5:  E=   -1056.6320522863 Eh  1.285 eV  10366.3 cm**-1
      0.45202 [     4]: 12000
      0.45194 [     8]: 10200
      0.05086 [    18]: 01110
      0.03439 [    19]: 01101
      0.00560 [    13]: 10002
      0.00519 [    11]: 10020
ROOT   6:  E=   -1056.6319354589 Eh  1.288 eV  10391.9 cm**-1
      0.45326 [     1]: 20100
      0.45006 [    14]: 02100
      0.04601 [     7]: 11001
      0.03992 [     6]: 11010
      0.00540 [    25]: 00120
```

```
      0.00534 [    27]: 00102
ROOT   7:  E=   -1056.6319347872 Eh  1.288 eV  10392.1 cm**-1
      0.45330 [     0]: 21000
      0.45001 [    17]: 01200
      0.04603 [    10]: 10101
      0.03992 [     9]: 10110
      0.00540 [    20]: 01020
      0.00534 [    22]: 01002
ROOT   8:  E=   -1056.5638097544 Eh  3.142 eV  25343.8 cm**-1
      0.74230 [     9]: 10110
      0.22587 [    10]: 10101
      0.00898 [    20]: 01020
      0.00776 [     0]: 21000
      0.00747 [    17]: 01200
      0.00730 [    21]: 01011
ROOT   9:  E=   -1056.5637823472 Eh  3.143 eV  25349.8 cm**-1
      0.74230 [     6]: 11010
      0.22589 [     7]: 11001
      0.00896 [    25]: 00120
      0.00775 [     1]: 20100
      0.00745 [    14]: 02100
      0.00733 [    26]: 00111
```

d^4: Orbital Occupation in $[MoH_6]^{4-}$

```
-------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 5 NROOTS= 5
-------------------------------------------

ROOT   0:  E=   -4089.0780399895 Eh
      0.99990 [     0]: 11110
ROOT   1:  E=   -4089.0720137956 Eh  0.164 eV   1322.6 cm**-1
      0.99990 [     1]: 11101
ROOT   2:  E=   -4088.8719081731 Eh  5.609 eV  45240.7 cm**-1
      1.00000 [     4]: 01111
ROOT   3:  E=   -4088.8715868630 Eh  5.618 eV  45311.2 cm**-1
      1.00000 [     3]: 10111
ROOT   4:  E=   -4088.8704582531 Eh  5.649 eV  45558.9 cm**-1
      1.00000 [     2]: 11011

-------------------------------------------
CAS-SCF STATES FOR BLOCK  2 MULT= 3 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -4089.1467239018 Eh
      0.99716 [     9]: 11200
ROOT   1:  E=   -4089.1458689564 Eh  0.023 eV    187.6 cm**-1
      0.99719 [     6]: 12100
ROOT   2:  E=   -4089.1456322491 Eh  0.030 eV    239.6 cm**-1
      0.99719 [     0]: 21100
ROOT   3:  E=   -4089.0519761189 Eh  2.578 eV  20794.7 cm**-1
      0.99543 [    10]: 11110
      0.00456 [    11]: 11101
ROOT   4:  E=   -4089.0445286908 Eh  2.781 eV  22429.3 cm**-1
      0.99060 [    11]: 11101
      0.00939 [    10]: 11110
ROOT   5:  E=   -4089.0167754883 Eh  3.536 eV  28520.4 cm**-1
      0.65259 [     7]: 12010
      0.29301 [    15]: 10210
      0.05095 [    16]: 10201
      0.00283 [     8]: 12001
ROOT   6:  E=   -4089.0164463845 Eh  3.545 eV  28592.6 cm**-1
      0.72045 [     1]: 21010
      0.24455 [    25]: 01210
      0.03430 [    26]: 01201
ROOT   7:  E=   -4089.0153271477 Eh  3.575 eV  28838.3 cm**-1
      0.52450 [     3]: 20110
      0.39778 [    22]: 02110
      0.05033 [     4]: 20101
      0.02675 [    23]: 02101
ROOT   8:  E=   -4089.0142884382 Eh  3.604 eV  29066.2 cm**-1
      0.96805 [    10]: 11110
      0.03153 [    11]: 11101
ROOT   9:  E=   -4089.0126883764 Eh  3.647 eV  29417.4 cm**-1
      0.98673 [    10]: 11110
      0.00990 [    11]: 11101

-------------------------------------------
CAS-SCF STATES FOR BLOCK  3 MULT= 1 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -4089.1100994878 Eh
      0.98358 [    13]: 11200
      0.00718 [     6]: 20101
      0.00625 [    28]: 02101
ROOT   1:  E=   -4089.1093071356 Eh  0.022 eV    173.9 cm**-1
      0.98294 [    10]: 12100
      0.00801 [    32]: 01210
      0.00555 [     3]: 21001
ROOT   2:  E=   -4089.1090788765 Eh  0.028 eV    224.0 cm**-1
      0.98280 [     1]: 21100
      0.00847 [    19]: 10210
      0.00417 [    12]: 12001
      0.00393 [    11]: 12010
ROOT   3:  E=   -4089.1074497560 Eh  0.072 eV    581.5 cm**-1
      0.55594 [    26]: 02200
      0.42842 [     4]: 20200
      0.00680 [     0]: 22000
      0.00396 [    14]: 11110
      0.00388 [    15]: 11101
ROOT   4:  E=   -4089.1061453128 Eh  0.108 eV    867.8 cm**-1
      0.63910 [     0]: 22000
```

```
      0.23718 [     4]: 20200
      0.11504 [    26]: 02200
      0.00390 [    15]: 11101
      0.00377 [    14]: 11110
ROOT   5:  E=   -4089.0585508846 Eh  1.403 eV  11313.6 cm**-1
      0.30099 [     0]: 22000
      0.28522 [     4]: 20200
      0.28085 [    26]: 02200
      0.07286 [    14]: 11110
      0.05902 [    15]: 11101
ROOT   6:  E=   -4089.0056928622 Eh  2.841 eV  22914.6 cm**-1
      0.50450 [     5]: 20110
      0.43066 [    27]: 02110
      0.04096 [    28]: 02101
      0.02209 [     6]: 20101
ROOT   7:  E=   -4089.0046843598 Eh  2.868 eV  23135.9 cm**-1
      0.87103 [    14]: 11110
      0.12496 [    15]: 11101
ROOT   8:  E=   -4089.0034439470 Eh  2.902 eV  23408.2 cm**-1
      0.66148 [     2]: 21010
      0.16565 [    32]: 01210
      0.09556 [    33]: 01201
      0.07562 [     3]: 21001
ROOT   9:  E=   -4089.0025160109 Eh  2.927 eV  23611.8 cm**-1
      0.63742 [    11]: 12010
      0.14821 [    19]: 10210
      0.13552 [    12]: 12001
      0.07714 [    20]: 10201
```

d^8: Orbital Occupation in $[NiH_6]^{4-}$

```
-------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 3 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -1529.5523828489 Eh
      1.00000 [     9]: 22211
ROOT   1:  E=   -1529.4883537793 Eh  1.742 eV  14052.8 cm**-1
      0.58731 [     7]: 22112
      0.41269 [     8]: 22121
ROOT   2:  E=   -1529.4883310071 Eh  1.743 eV  14057.8 cm**-1
      0.87872 [     5]: 21212
      0.12128 [     6]: 21221
ROOT   3:  E=   -1529.4882952417 Eh  1.744 eV  14065.6 cm**-1
      0.97031 [     3]: 12221
      0.02969 [     2]: 12212
ROOT   4:  E=   -1529.4488437597 Eh  2.817 eV  22724.2 cm**-1
      0.44427 [     8]: 22121
      0.31275 [     7]: 22112
      0.24297 [     0]: 11222
ROOT   5:  E=   -1529.4486613719 Eh  2.822 eV  22764.2 cm**-1
      0.66276 [     6]: 21221
      0.24535 [     1]: 12122
      0.09190 [     5]: 21212
ROOT   6:  E=   -1529.4483796474 Eh  2.830 eV  22826.1 cm**-1
      0.72854 [     2]: 12212
      0.24909 [     4]: 21122
      0.02237 [     3]: 12221
ROOT   7:  E=   -1529.3779706456 Eh  4.746 eV  38279.1 cm**-1
      0.75091 [     4]: 21122
      0.24177 [     2]: 12212
      0.00732 [     3]: 12221
ROOT   8:  E=   -1529.3778781925 Eh  4.749 eV  38299.3 cm**-1
      0.75465 [     1]: 12122
      0.21596 [     6]: 21221
      0.02939 [     5]: 21212
ROOT   9:  E=   -1529.3778165088 Eh  4.750 eV  38312.9 cm**-1
      0.75703 [     0]: 11222
      0.14304 [     8]: 22121
      0.09993 [     7]: 22112
-------------------------------------------
CAS-SCF STATES FOR BLOCK  2 MULT= 1 NROOTS=10
-------------------------------------------

ROOT   0:  E=   -1529.4887435809 Eh
      0.44347 [    14]: 22220
      0.43076 [    12]: 22202
      0.11660 [    13]: 22211
      0.00626 [     0]: 02222
ROOT   1:  E=   -1529.4887392004 Eh  0.000 eV      1.0 cm**-1
      0.87416 [    13]: 22211
      0.05927 [    12]: 22202
      0.05736 [    14]: 22220
      0.00469 [     5]: 20222
      0.00452 [     9]: 22022
ROOT   2:  E=   -1529.4404428030 Eh  1.314 eV  10600.8 cm**-1
      0.46823 [    12]: 22202
      0.45771 [    14]: 22220
      0.02503 [     9]: 22022
      0.02473 [     5]: 20222
      0.02427 [     0]: 02222
ROOT   3:  E=   -1529.4195552200 Eh  1.883 eV  15185.1 cm**-1
      0.56724 [    10]: 22112
      0.40200 [    11]: 22121
      0.03076 [     1]: 11222
ROOT   4:  E=   -1529.4194898705 Eh  1.884 eV  15199.4 cm**-1
      0.84943 [     7]: 21212
      0.11970 [     8]: 21221
      0.03087 [     2]: 12122
ROOT   5:  E=   -1529.4193902695 Eh  1.887 eV  15221.3 cm**-1
      0.93976 [     4]: 12221
      0.03105 [     6]: 21122
      0.02920 [     3]: 12212
ROOT   6:  E=   -1529.3969315978 Eh  2.498 eV  20150.4 cm**-1
      0.58538 [    11]: 22121
      0.41461 [    10]: 22112
ROOT   7:  E=   -1529.3966460463 Eh  2.506 eV  20213.1 cm**-1
      0.87664 [     8]: 21221
```

```
      0.12335 [     7]: 21212
ROOT   8:  E=   -1529.3962023090 Eh  2.518 eV  20310.5 cm**-1
      0.96990 [     3]: 12212
      0.03010 [     4]: 12221
ROOT   9:  E=   -1529.3196627317 Eh  4.601 eV  37109.0 cm**-1
      0.59546 [     9]: 22022
      0.36928 [     5]: 20222
      0.02604 [     0]: 02222
      0.00903 [    13]: 22211
```

References

1. Neese, F. (2012). The ORCA program system, *WIREs Comput. Mol. Sci.*, **2**(1), 73–78. https://doi.org/10.1002/wcms.81.
2. Pantazis, D. A., Chen, X.-Y., Landis, C. R. & Neese, F. (2008). All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms, *J. Chem. Theory Comput.*, **4**(6), 908–919. https://doi.org/10.1021/ct800047t.
3. van Lenthe, E., Baerends, E. J. & Snijders, J. G. (1993). Relativistic regular two-component Hamiltonians, *J. Chem. Phys.*, **99**(6), 4597–4610. https://doi.org/10.1063/1.466059.
4. van Wüllen, C. (1998). Molecular density functional calculations in the regular relativistic approximation: Method, application to coinage metal diatomics, hydrides, fluorides and chlorides, and comparison with first-order relativistic calculations, *J. Chem. Phys.*, **109**(2), 392–399. https://doi.org/10.1063/1.476576.
5. Sinnecker, S., Rajendran, A., Klamt, A., Diedenhofen, M. & Neese, F. (2006). Calculation of solvent shifts on electronic g-tensors with the conductor-like screening model (COSMO) and its self-consistent generalization to real solvents (direct COSMO-RS), *J. Phys. Chem. A,* **110**(6), 2235–2245. https://doi.org/10.1021/jp056016z.
6. Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **98**(7), 5648–5652. https://doi.org/10.1063/1.464913.
7. Weigend, F. & Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn. Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, **7**(18), 3297–3305. https://doi.org/10.1039/B508541A.
8. Weigend, F. (2006). Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.*, **8**(9), 1057–1065. https://doi.org/10.1039/b515623h.
9. Kossmann, S. & Neese, F. (2009). Comparison of two efficient approximate Hartee–Fock approaches, *Chem. Phys. Lett.*, **481**(4-6), 240–243. https://doi.org/10.1016/j.cplett.2009.09.073.
10. Izsák, R. & Neese, F. (2011). An overlap fitted chain of spheres exchange method, *J. Chem. Phys.*, **135**(14), 144105. https://doi.org/10.1063/1.3646921.
11. Grimme, S., Ehrlich, S. & Goerigk, L. (2011). Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, **32**(7), 1456–1465. https://doi.org/10.1002/jcc.21759.
12. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.*, **132**(15), 154104. https://doi.org/10.1063/1.3382344.
13. Weigend, F. (2008). Hartree-Fock exchange fitting basis sets for H to Rn, *J. Comput. Chem.*, **29**(2), 167–175. https://doi.org/10.1002/jcc.20702.
14. Stoychev, G. L., Auer, A. A. & Neese, F. (2017). Automatic Generation of Auxiliary Basis Sets, *J. Chem. Theory Comput.*, **13**(2), 554–562. https://doi.org/10.1021/acs.jctc.6b01041.
15. Weigend, F., Kattannek, M. & Ahlrichs, R. (2009). Approximated electron repulsion integrals. Cholesky decomposition versus resolution of the identity methods, *J. Chem. Phys.*, **130**(16), 164106. https://doi.org/10.1063/1.3116103.