# Electronic supplementary information (ESI): Core-electron contributions to the magnetic response of molecules with heavy elements and their significance in aromaticity assessments

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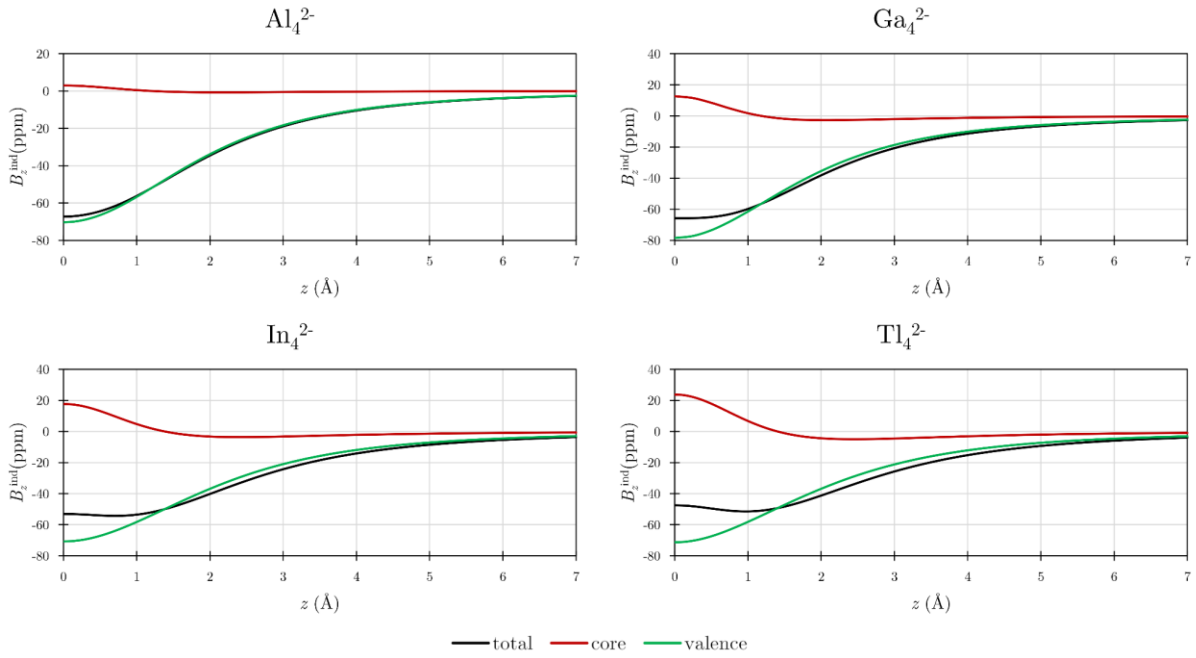


**Figure S1.** The *z*-profiles of the total, RVE core, and valence contributions to $B^{ind}_z$ for the $E_4^{2-}$ (E=Al, Ga, In, Tl) clusters computed at the BHandHLYP/x2c-TZVPall-2c level.

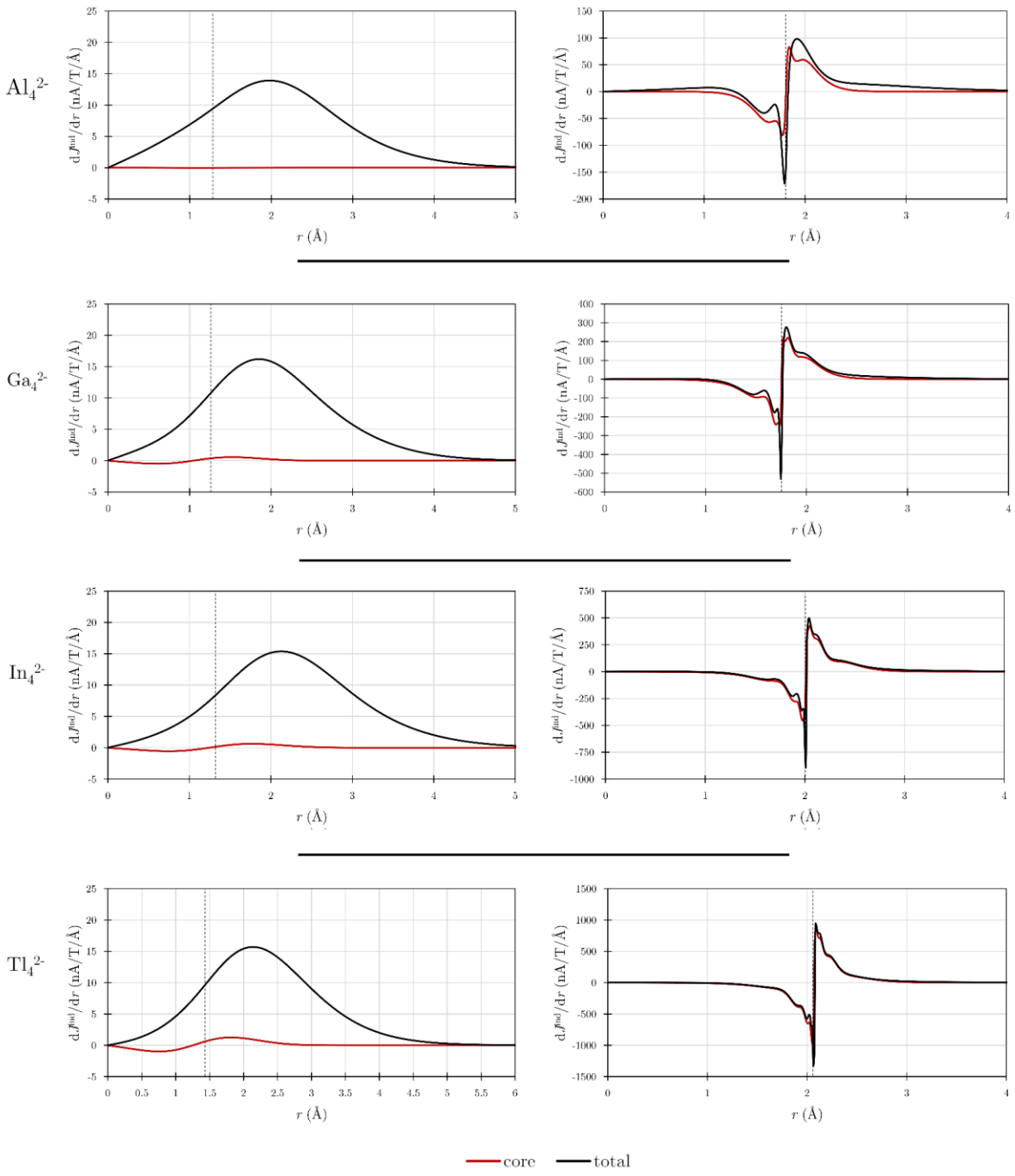


**Figure S2.** The ring-current strength profiles of the RVE core-electron contribution and total (all-electron) $\mathrm{d}J^{\mathrm{ind}}/\mathrm{d}r$ resulting using a plane that intersects a E-E bond (left) and a E nucleus (right) for the $E_4^{2-}$ (E=Al, Ga, In, Tl) clusters calculated at the BHandHLYP/x2c-TZVPall-2c level. The vertical dotted lines show the $r$ values corresponding to the intersection with the atoms. Integrating the area under the red curve of one of the peaks yields to the atomic current strength, which is 18.82, 50.73, 81.62, and 134.03 nA/T for Al, Ga, In and Tl, respectively.

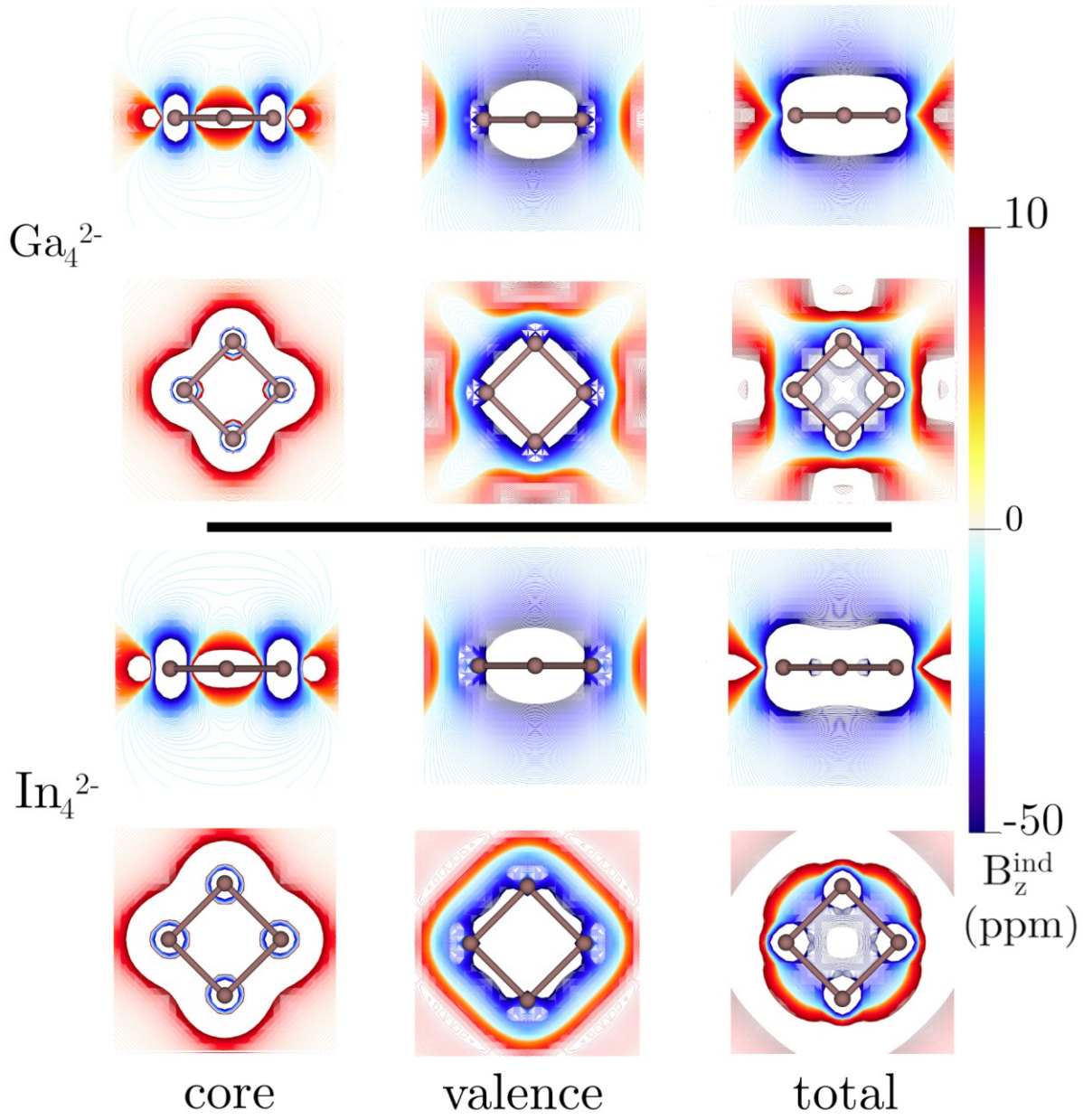


**Figure S3.** Isolines of the core, valence, and total contributions to $B^{ind}_z$ of $Ga_4^{2-}$ and $In_4^{2-}$ plotted on (top) and in a slide orthogonal (bottom) to the molecular plane calculated at the BHandHLYP/x2c-TZVPall-2c level.

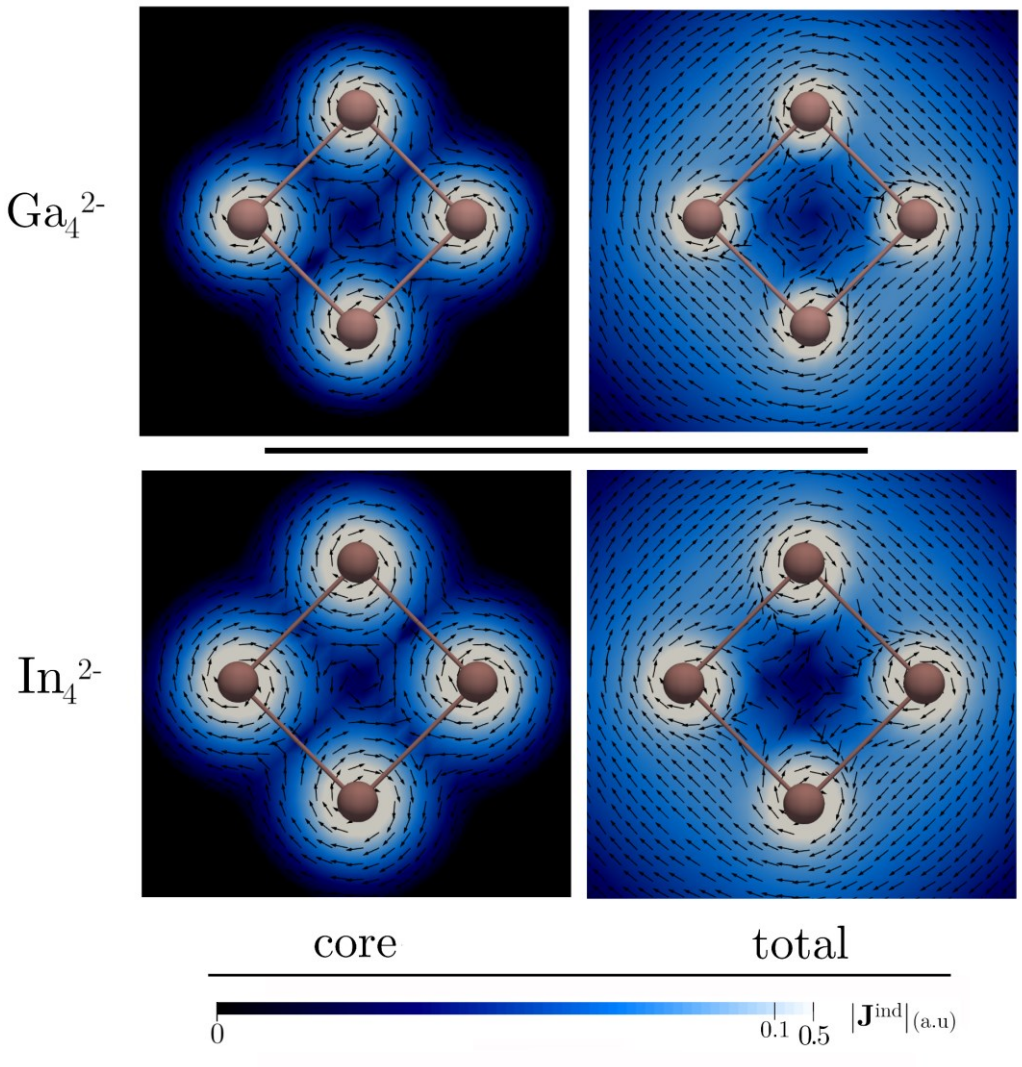


**Figure S4.** Plots of the total and the core-electron contribution to $\mathbf{J}^{ind}$ maps for $Ga_4^{2-}$ and $In_4^{2-}$ calculated at the BHandHLYP/x2c-TZVPall-2c level.

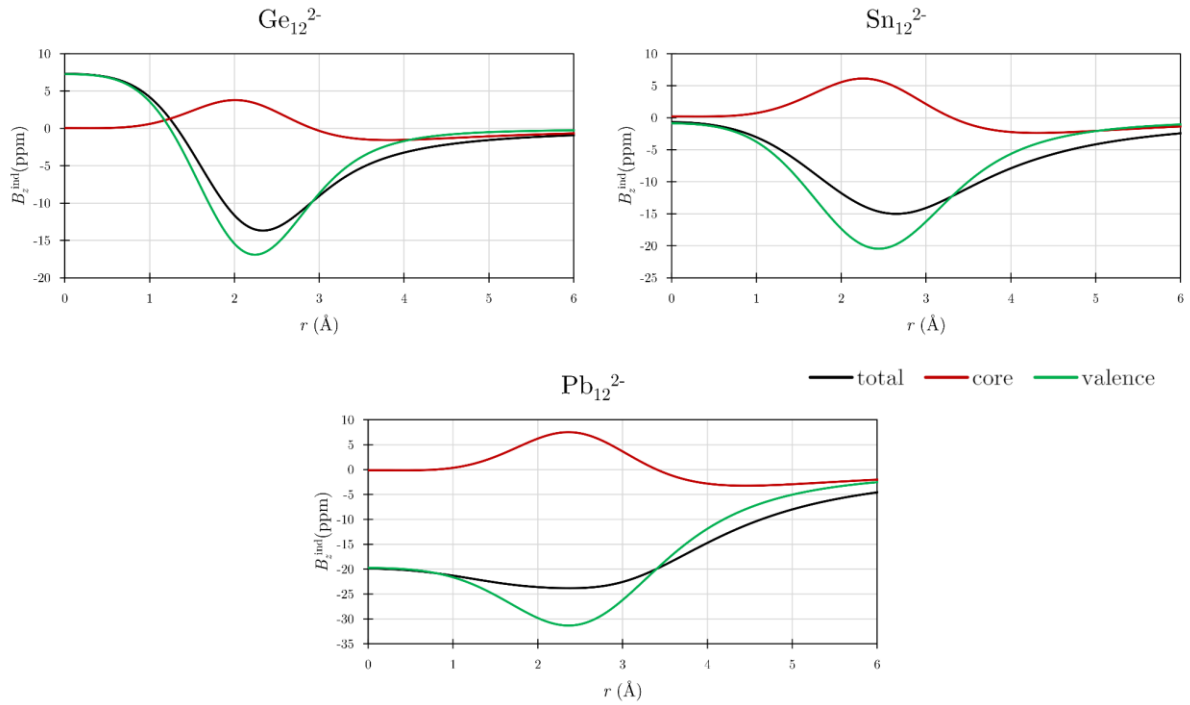


**Figure S5.** The *r*-profiles of the total, RVE core, and valence contributions to $B^{ind}{}_z$ for the $M_{12}{}^{2-}$ clusters computed at the BHandHLYP/x2c-TZVPall-2c level. The radial *r* coordinate runs from the cage center (*r*=0), intersects a three-membered face ring, and ends where $B^{ind}{}_z$ vanishes. The external magnetic field points parallel to the *z* axis ($C_5$ axis).

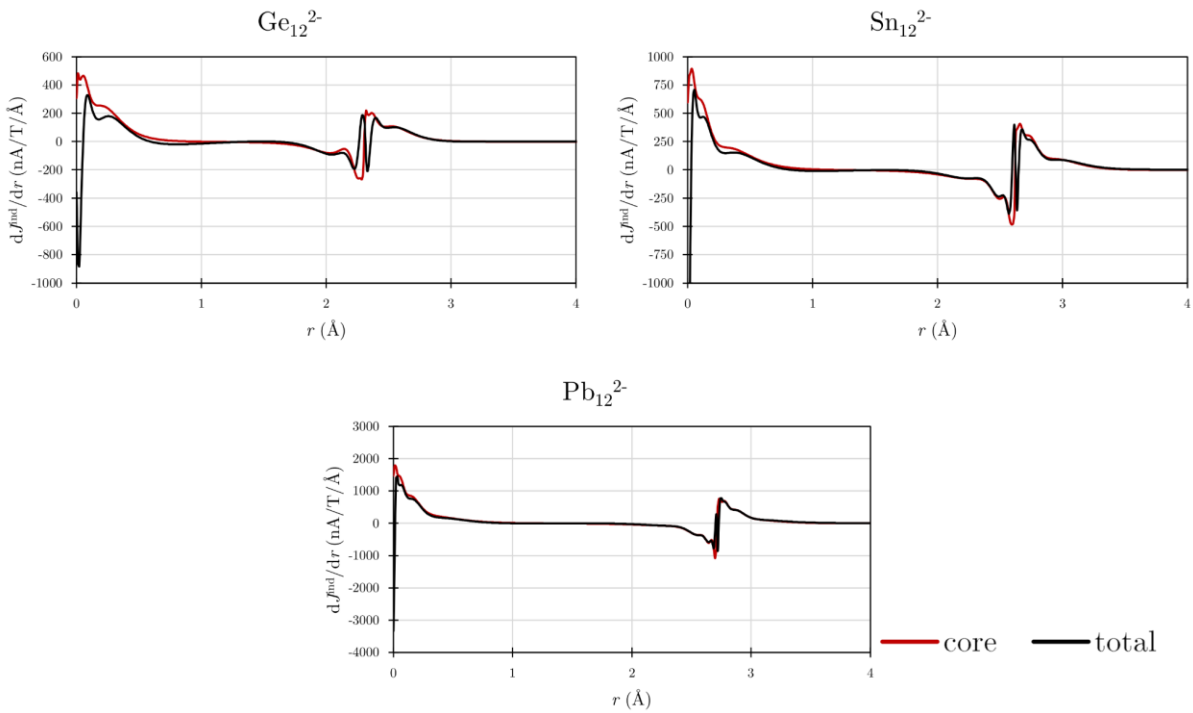


**Figure S6.** The ring-current strength profiles of the RVE core-electron contribution and total (all-electron) $dJ^{ind}/dr$ resulting using a plane that intersects the surface of the $M_{12}{}^{2-}$ clusters

calculated at the BHandHLYP/x2c-TZVPall-2c level. Integrating the area under the curves leads to the ring-currents strengths.

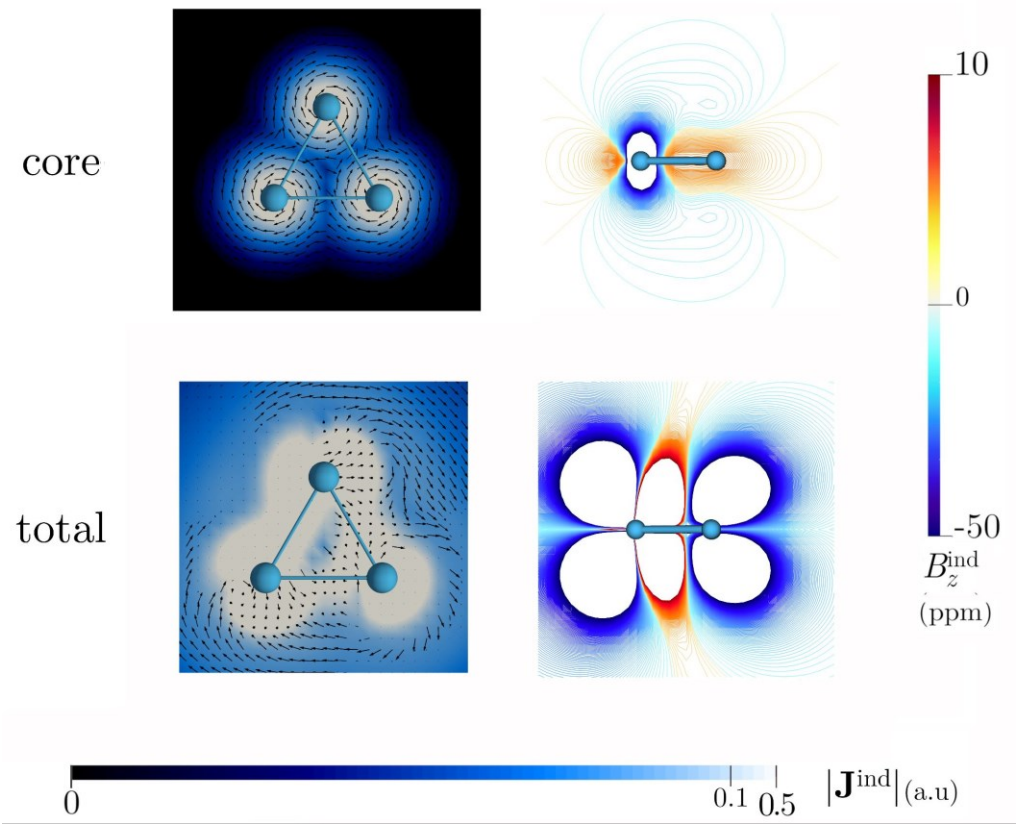


**Figure S7.** Plots of the total and the core-electron contribution to $\mathbf{J}^{ind}$ (left) and $B^{ind}{}_z$ (right) maps and for the singlet structure of $Hf_3$ calculated at the BHandHLYP/x2c-TZVPall-2c level.

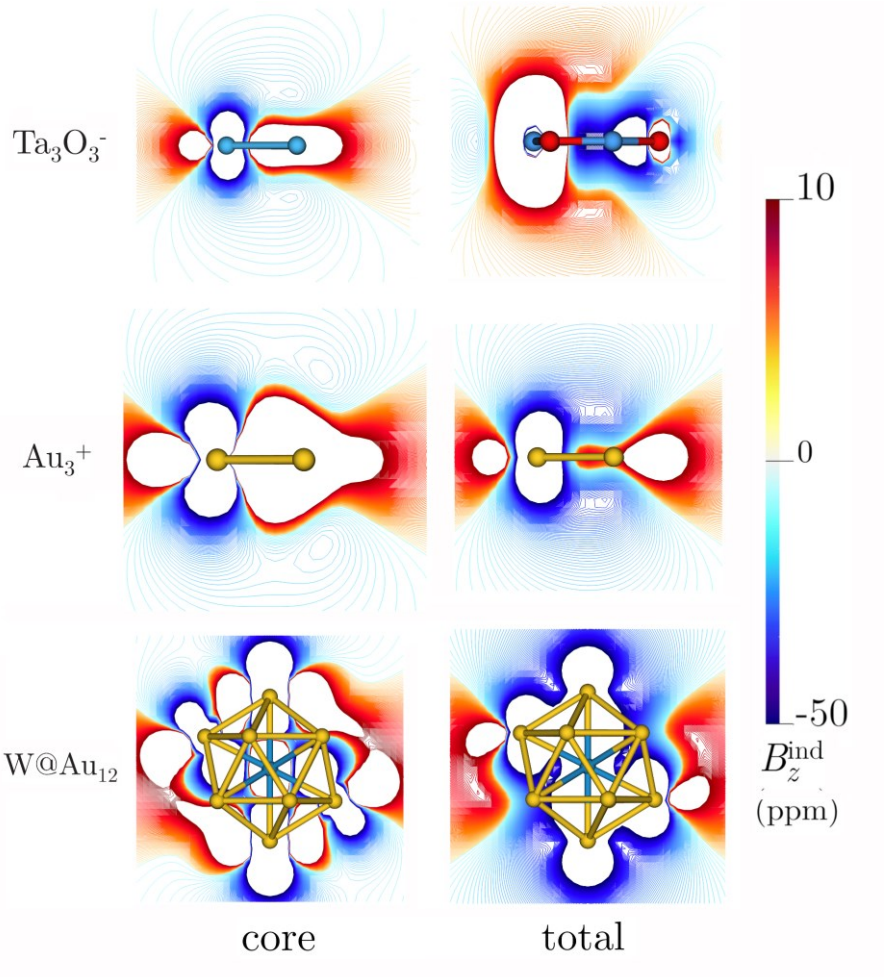


**Figure S8.** Isolines of the total and core-electron contribution to $B^{ind}_z$ for $Ta_3O_3^-$, $Au_3^+$, and W@$Au_{12}$ clusters calculated at the BHandHLYP/x2c-TZVPall-2c level. The core-electron isolines are unreliable because the RVE approximation is not well defined in these systems (see main text).

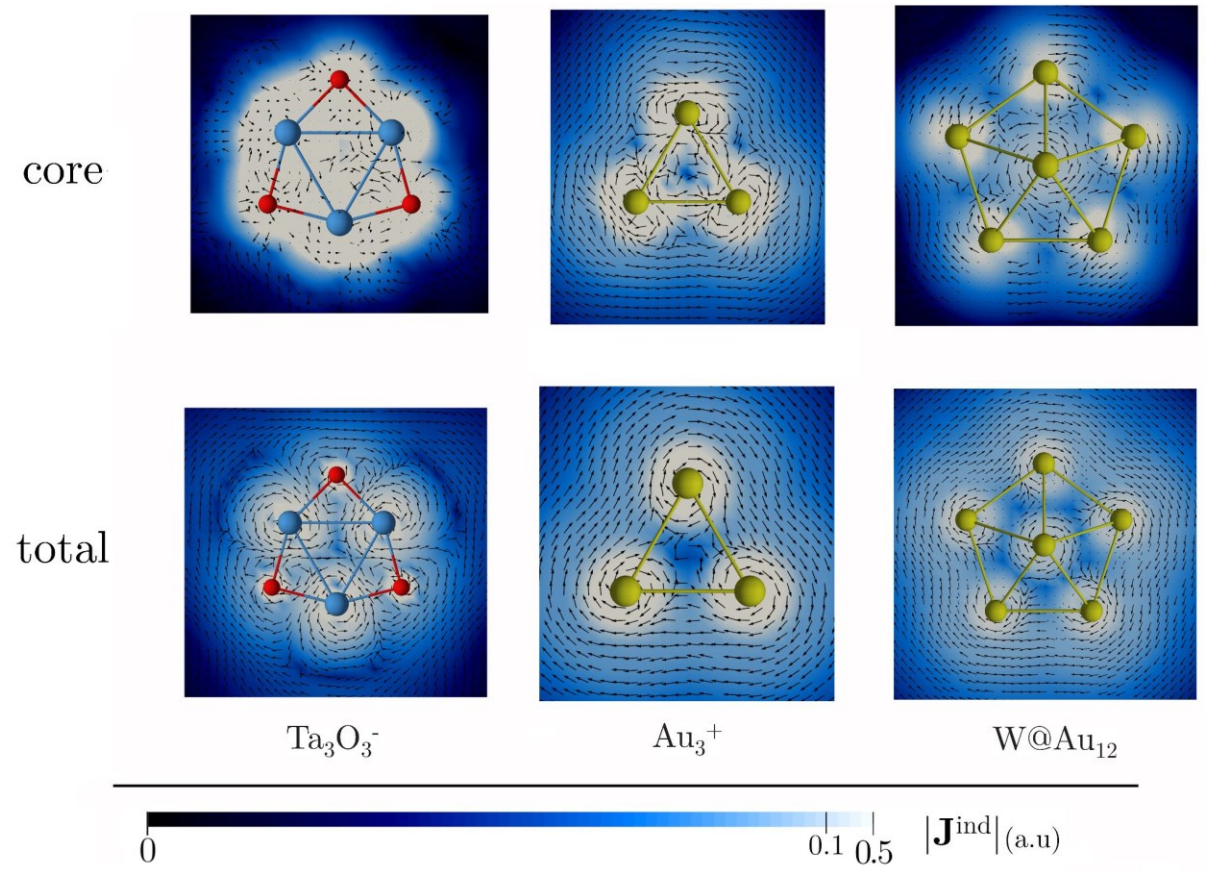


**Figure S9.** Plots of the total and the core-electron contribution to $\mathbf{J}^{ind}$ maps for $Ta_3O_3^-$, $Au_3^+$, and $W@Au_{12}$ clusters calculated at the BHandHLYP/x2c-TZVPall-2c level. The core-electron maps are unreliable because the RVE approximation is not well defined in these systems (see main text).

**Table S1.** Delocalization indices (DI) dissected into its core and valence contribution for icosahedral $M_{12}^{2-}$ clusters computed at the BHandHLYP/x2c-TZVPall-2c level. The reported values correspond to the three equivalent bonds connecting adjacent atoms in the molecule. The valence contribution is estimated by subtracting the core-electron response from the total.

| Molecule | Contribution | DI (in the different M-M bonds) | | |
|---|---|---|---|---|
| $Ge_{12}^{2-}$ | Total | 0.566 | 0.566 | 0.566 |
| | Core | 0.018 | 0.018 | 0.018 |
| | Valence | 0.548 | 0.548 | 0.548 |
| $Sn_{12}^{2-}$ | Total | 0.569 | 0.569 | 0.569 |
| | Core | 0.024 | 0.024 | 0.024 |

| | | | | |
|---|---|---|---|---|
| | Valence | 0.545 | 0.545 | 0.545 |
| $Pb_{12}^{2-}$ | Total | 0.566 | 0.566 | 0.566 |
| | Core | 0.046 | 0.046 | 0.046 |
| | Valence | 0.520 | 0.520 | 0.520 |

**Table S2.** Delocalization indices (DI) dissected into its core and valence contribution for $Hf_3$ (triplet/singlet), Pt-benzene-Cp, and $SrCs_5^+$ clusters computed at the BHandHLYP/x2c-TZVPall-2c level. The reported values correspond to equivalent bonds connecting adjacent atoms in the molecule. The valence contribution is estimated by subtracting the core-electron response from the total.

| Molecule | Contribution | DI (in the different bonds) |
|---|---|---|
| $Hf_3$ | Total | 1.860/2.191 |
| | Core | 0.059/0.059 |
| | Valence | 1.801/2.132 |
| Pt-benzene-Cp | Total | 1.454, 1.354 in C-C<br>1.287 in Pt-C |
| | Core | 0.000, 0.000 in C-C<br>0.000, 0.000 in Pt-C |
| | Valence | 1.454, 1.354 in C-C<br>1.287 in Pt-C |
| Osmapyridinium | Total | 1.258, 1.460, 1.304 in C-C<br>1.304 in N-C<br>1.390 in Os-C<br>0.992 in Os-N |
| | Core | 0.000, 0.000, 0.000 in C-C<br>0.000 in N-C<br>0.001 in Os-C<br>0.002 in Os-N |
| | Valence | 1.258, 1.460, 1.304 in C-C<br>1.304 in N-C<br>1.389 in Os-C<br>0.990 in Os-N |

| | | |
|---|---|---|
| Osmapentalene (monocation) | Total | 1.4818, 1.2974, 1.3519 in C-C<br>1.1716, 0.8344 in Os-C |
| | Core | 0.000, 0.000, 0.000, in C-C<br>0.001, 0.001 in Os-C |
| | Valence | 1.4818, 1.2974, 1.3519 in C-C<br>1.1706, 0.8334 in Os-C |
| $SrCs_5^+$ | Total | 0.000, 0.000, 0.000, in C-C<br>0.001, 0.001 in Os-C |
| | Core | 0.000 in Cs-Cs<br>0.000 in Sr-Cs |
| | Valence | 0.104 in Cs-Cs<br>0.541 in Sr-Cs |
| $Ge_9^{4-}$ | Total | 0.6581, 0.7377, 0.2427, 0.7378 |
| | Core | 0.0204, 0.0205, 0.0043, 0.0228 |
| | Valence | 0.6377,0.7172,0.2384,0.715 |

**Table S3.** Delocalization indices and electronic aromaticity indices dissected into its core and valence contribution for $Hf_3$ (triplet/singlet), Pt-benzene, osmapyridinium, osmapentalene (monocation), $SrCs_5^+$ clusters computed at the BHandHLYP/x2c-TZVPall-2c level. The valence contribution is estimated by subtracting the core-electron response from the total.

| Index | Contribution | $Hf_3$ | Pt-benzene | osmapyridinium | osmapentalene (monocation) | $SrCs_5^+$ |
|---|---|---|---|---|---|---|
| $I_{ring}$ | Total | 0.423/0.982 | 0.027 | 0.022 | 0.005 | 0.000 |
| | Core | 0.000/0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| | Valence | 0.423/0.982 | 0.027 | 0.022 | 0.005 | 0.000 |
| MCI | Total | 0.423/0.982 | 0.042 | 0.031 | 0.002 | 0.000 |
| | Core | 0.000/0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| | Valence | 0.423/0.982 | 0.042 | 0.031 | 0.002 | 0.000 |

**Table S4.** Delocalization indices and electronic aromaticity indices dissected into its core RVE contribution for $Ta_3O_3^-$, $Au_3^+$, W@$Au_{12}$, and $K_2[Th(C_8H_8)Cl_2]_3$ clusters computed at the BHandHLYP/x2c-TZVPall-2c level. For the case of $K_2[Th(C_8H_8)Cl_2]_3$, all calculations were done on a BHandHLYP level with an x2c-TZVPall-2c basis for all atoms except for Th, which a Stuttgart-Bonn relativistic effective-core potential and the associated segmented valence basis sets for thorium were used, using the geometry reported in *Angew. Chem. Int. Ed Engl.*, 2022, 61, e202204337, using the Gaussian 16 program. The core-electron maps are unreliable because the RVE approximation is not well defined in these systems (see main text).

| Index | Contribution | $Ta_3O_3^-$ | $Au_3^+$ | W@$Au_{12}$ | $K_2[Th(C_8H_8)Cl_2]_3$ |
|---|---|---|---|---|---|
| DI | Total | 1.087 in Ta-Ta<br>0.978 in Ta-O | 0.807 | 0.421, 0.421, 0.421 in Au-Au<br>0.559, 0.559 in Au-W | 0.271 in Th-Th |
| | Core | 0.078 in Ta-Ta<br>0.344 in Ta-O | 0.603 | 0.447, 0.395, 0.446 in Au-Au<br>0.539, 0.583 in Au-W | - |
| $I_{ring}$ | Total | 0.000 | 0.144 | - | 0.070 |
| | Core | -0.012 | -0.026 | - | - |
| MCI | Total | 0.001 | 0.144 | - | 0.134 |
| | Core | -0.002 | -0.026 | - | - |

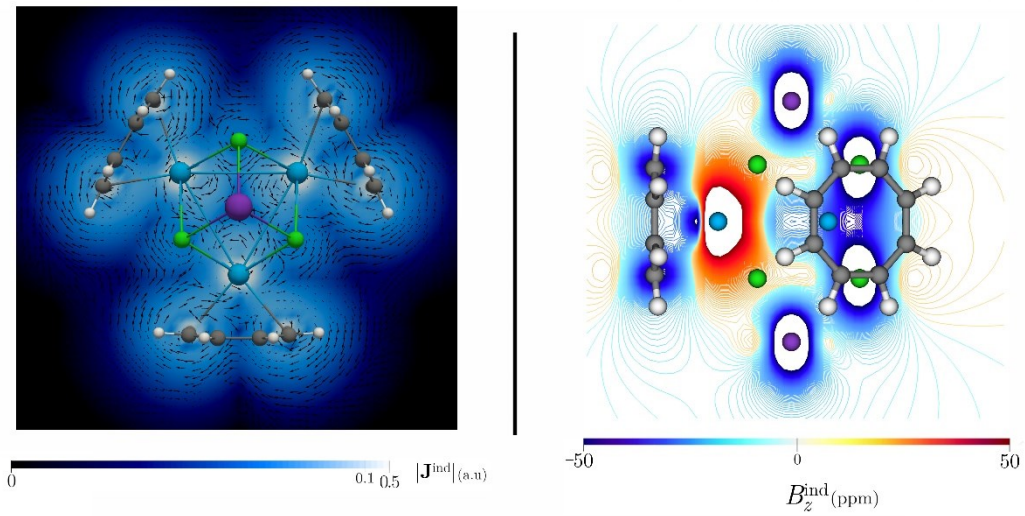


**Figure S10.** Plots of the total $\mathbf{J}^{ind}$ map (left) and $B^{ind}{}_z$ (right) for $K_2[Th(C_8H_8)Cl_2]_3$, all calculations were done on a BHandHLYP level with an x2c-TZVPall-2c basis for all atoms except for Th, which a Stuttgart-Bonn relativistic effective-core potential and the associated

segmented valence basis sets for thorium were used, using the geometry reported in *Angew. Chem. Int. Ed Engl.*, 2022, 61, e202204337, using the Gaussian 16 program.

Molecular geometries optimized at the TPSS-D3(BJ)/x2c-TZVPall-2c level incorporating the two-component relativistic treatment and spin-orbit interactions.

$Al_4^{2-}$

| | | | |
|---|---|---|---|
| Al | 1.816158513 | 0.000000000 | 0.000000000 |
| Al | 0.000000000 | -1.816158513 | 0.000000000 |
| Al | 0.000000000 | 1.816158513 | 0.000000000 |
| Al | -1.816158513 | 0.000000000 | 0.000000000 |

$Ga_4^{2-}$

| | | | |
|---|---|---|---|
| Ga | 1.757892914 | 0.000000000 | 0.000000000 |
| Ga | 0.000000000 | -1.757892914 | 0.000000000 |
| Ga | 0.000000000 | 1.757892914 | 0.000000000 |
| Ga | -1.757892914 | 0.000000000 | 0.000000000 |

$In_4^{2-}$

| | | | |
|---|---|---|---|
| In | 2.015259842 | 0.000000000 | 0.000000000 |
| In | 0.000000000 | -2.015259842 | 0.000000000 |
| In | 0.000000000 | 2.015259842 | 0.000000000 |
| In | -2.015259842 | 0.000000000 | 0.000000000 |

$Tl_4^{2-}$

| | | | |
|---|---|---|---|
| Tl | 2.075944594 | 0.000000000 | 0.000000000 |
| Tl | 0.000000000 | -2.075944594 | 0.000000000 |
| Tl | 0.000000000 | 2.075944594 | 0.000000000 |
| Tl | -2.075944594 | 0.000000000 | 0.000000000 |

$Ge_{12}^{2-}$

| | | | |
|---|---|---|---|
| Ge | 1.868138500 | 1.357282100 | 1.154573100 |
| Ge | 0.000000000 | 0.000000000 | 2.581703900 |
| Ge | -1.868138500 | -1.357282100 | -1.154573100 |
| Ge | -2.309146200 | 0.000000000 | 1.154573100 |
| Ge | 1.868138500 | -1.357282100 | 1.154573100 |
| Ge | -0.713565400 | -2.196128500 | 1.154573100 |
| Ge | 0.000000000 | 0.000000000 | -2.581703900 |
| Ge | 0.713565400 | -2.196128500 | -1.154573100 |
| Ge | 0.713565400 | 2.196128500 | -1.154573100 |
| Ge | -0.713565400 | 2.196128500 | 1.154573100 |
| Ge | -1.868138500 | 1.357282100 | -1.154573100 |
| Ge | 2.309146200 | 0.000000000 | -1.154573100 |

$Sn_{12}^{2-}$

| | | | |
|---|---|---|---|
| Sn | 0.810998200 | 2.495995700 | -1.312222600 |
| Sn | 0.000000000 | 0.000000000 | -2.934219000 |
| Sn | -0.810998200 | -2.495995700 | 1.312222600 |
| Sn | 0.810998200 | -2.495995700 | -1.312222600 |
| Sn | -2.123220800 | 1.542610200 | -1.312222600 |
| Sn | -2.123220800 | -1.542610200 | -1.312222600 |
| Sn | 0.000000000 | 0.000000000 | 2.934219000 |
| Sn | -2.624445200 | 0.000000000 | 1.312222600 |
| Sn | 2.123220800 | 1.542610200 | 1.312222600 |
| Sn | 2.624445200 | 0.000000000 | -1.312222600 |
| Sn | 2.123220800 | -1.542610200 | 1.312222600 |
| Sn | -0.810998200 | 2.495995700 | 1.312222600 |

$Pb_{12}^{2-}$

| | | | |
|---|---|---|---|
| Pb | 2.199736000 | 1.598201800 | 1.359511600 |
| Pb | 0.000000000 | 0.000000000 | 3.039960400 |
| Pb | -2.199736000 | -1.598201800 | -1.359511600 |
| Pb | -2.719023300 | 0.000000000 | 1.359511600 |
| Pb | 2.199736000 | -1.598201800 | 1.359511600 |
| Pb | -0.840224400 | -2.585944800 | 1.359511600 |
| Pb | 0.000000000 | 0.000000000 | -3.039960400 |
| Pb | 0.840224400 | -2.585944800 | -1.359511600 |
| Pb | 0.840224400 | 2.585944800 | -1.359511600 |
| Pb | -0.840224400 | 2.585944800 | 1.359511600 |
| Pb | -2.199736000 | 1.598201800 | -1.359511600 |
| Pb | 2.719023300 | 0.000000000 | -1.359511600 |

$Hf_3$ (triplet)

| | | | |
|---|---|---|---|
| Hf | 0.771620500 | 1.336485800 | 0.000000000 |
| Hf | 0.771620500 | -1.336485800 | 0.000000000 |
| Hf | -1.543240900 | 0.000000000 | 0.000000000 |

Hf (singlet)

| | | | |
|---|---|---|---|
| Hf | 0.766281639 | 1.327084779 | 0.000000000 |
| Hf | 0.766289202 | -1.327089118 | 0.000000000 |
| Hf | -1.532570840 | 0.000004339 | 0.000000000 |

Pt-benzene

| | | | |
|---|---|---|---|
| C | 2.046962213 | 0.990207305 | 0.710981450 |
| C | 2.043508388 | -0.375775388 | 1.154210382 |
| C | 2.054601133 | -1.214995323 | 0.000000000 |
| C | 2.043508388 | -0.375775388 | -1.154210382 |
| C | 2.046962213 | 0.990207305 | -0.710981450 |
| Pt | 0.082687451 | -0.001625862 | 0.000000000 |
| H | 2.050022614 | -2.295899834 | 0.000000000 |
| H | 2.034886010 | -0.707249956 | 2.182675955 |
| H | 2.041078839 | 1.861615431 | 1.350284596 |
| H | 2.034886010 | -0.707249956 | -2.182675955 |

| | | | |
|---|---|---|---|
| H | 2.041078839 | 1.861615431 | -1.350284596 |
| C | -1.308744108 | 1.353323407 | 0.000000000 |
| C | -1.313400745 | -1.353419872 | 0.000000000 |
| C | -2.685475263 | 1.231320147 | 0.000000000 |
| C | -2.689452567 | -1.225120213 | 0.000000000 |
| C | -3.356143116 | 0.004320846 | 0.000000000 |
| H | -0.926531363 | 2.378958836 | 0.000000000 |
| H | -3.286818371 | 2.140297627 | 0.000000000 |
| H | -4.444409585 | 0.006134346 | 0.000000000 |
| H | -3.294562851 | -2.131669982 | 0.000000000 |
| H | -0.937656989 | -2.381277784 | 0.000000000 |

Osmapyridinium

| | | | |
|---|---|---|---|
| Os | 0.037645000 | 0.033988500 | 0.000000000 |
| P | -0.804015100 | 0.002636900 | 2.158517300 |
| Cl | -1.689182400 | 1.805486100 | 0.000000000 |
| Cl | -1.430954200 | -2.049921300 | 0.000000000 |
| N | 1.471668800 | -1.304902600 | 0.000000000 |
| H | 1.136908200 | -2.275695900 | 0.000000000 |
| P | -0.804015100 | 0.002636900 | -2.158517300 |
| C | 2.761623400 | 1.291783200 | 0.000000000 |
| C | 2.791955900 | -1.176019200 | 0.000000000 |
| C | 3.429024900 | 0.078132400 | 0.000000000 |
| C | 1.350046600 | 1.453065000 | 0.000000000 |
| H | 1.024317400 | 2.502061300 | 0.000000000 |
| H | -0.641304500 | 1.152728900 | 2.955117500 |
| H | -2.190048600 | -0.174925000 | 2.197085300 |
| H | -0.374399500 | -0.996589900 | 3.059499200 |
| H | -0.641304500 | 1.152728900 | -2.955117500 |
| H | -0.374399500 | -0.996589900 | -3.059499200 |
| H | -2.190048600 | -0.174925000 | -2.197085300 |
| H | 3.380880700 | 2.189824000 | 0.000000000 |
| H | 4.515584900 | 0.074166000 | 0.000000000 |
| H | 3.387036400 | -2.086760100 | 0.000000000 |

Osmapentalene (cation +1)

| | | | |
|---|---|---|---|
| Os | -0.226640660 | 0.000000658 | -0.000000131 |
| P | -0.194257656 | -0.003475539 | 2.371239985 |
| C | 0.396049174 | -1.869511322 | 0.058700579 |
| C | 1.695801612 | -2.313828651 | 0.097713051 |
| C | 2.587617165 | -1.231949493 | 0.058983390 |
| H | 3.670487050 | -1.335630159 | 0.073175433 |
| C | 1.930712038 | 0.000006378 | 0.000000672 |
| C | 2.587618511 | 1.231922114 | -0.058979513 |
| H | 3.670489524 | 1.335624436 | -0.073171415 |
| Cl | -2.553650757 | -0.000000153 | -0.000001549 |
| H | -1.323404971 | -0.509595603 | 3.041110939 |
| H | 0.841618687 | -0.742903063 | 2.968543577 |
| H | -0.037331721 | 1.240195634 | 3.009086862 |
| C | 0.396021406 | 1.869501298 | -0.058698818 |

| | | | |
|---|---|---|---|
| C | 1.695828065 | 2.313860078 | -0.097712872 |
| H | -0.489502899 | 2.518731806 | -0.047402694 |
| P | -0.194254064 | 0.003472816 | -2.371240141 |
| H | -0.037325299 | -1.240199065 | -3.009085402 |
| H | -1.323401147 | 0.509590263 | -3.041113700 |
| H | 0.841622191 | 0.742901047 | -2.968542910 |
| H | 1.982986863 | -3.359753705 | 0.143547411 |
| H | 1.982987413 | 3.359734609 | -0.143544148 |
| H | -0.489513320 | -2.518737330 | 0.047402307 |

$SrCs_5^+$

| | | | |
|---|---|---|---|
| Cs | 1.464917700 | 4.508553200 | 0.000000000 |
| Cs | 1.464917700 | -4.508553200 | 0.000000000 |
| Cs | -3.835204400 | 2.786439100 | 0.000000000 |
| Cs | -3.835204400 | -2.786439100 | 0.000000000 |
| Cs | 4.740573400 | 0.000000000 | 0.000000000 |
| Sr | 0.000000000 | 0.000000000 | 0.000000000 |

$Ge_9^{4-}$

| | | | |
|---|---|---|---|
| Ge | 1.580424500 | 0.000000000 | -1.528060800 |
| Ge | 1.580424500 | 1.323339400 | 0.764030300 |
| Ge | 1.580424500 | -1.323339400 | 0.764030300 |
| Ge | -1.580424500 | 0.000000000 | -1.528060800 |
| Ge | -1.580424500 | -1.323339400 | 0.764030300 |
| Ge | -1.580424500 | 1.323339400 | 0.764030300 |
| Ge | 0.000000000 | -2.040468200 | -1.178064800 |
| Ge | 0.000000000 | 2.040468200 | -1.178064800 |
| Ge | 0.000000000 | 0.000000000 | 2.356129600 |

$Bi_4^{4+}$

| | | | |
|---|---|---|---|
| Bi | 0.000000000 | 1.550121800 | 0.000000000 |
| Bi | 3.051391600 | 0.000000000 | 0.000000000 |
| Bi | 0.000000000 | -1.550121800 | 0.000000000 |
| Bi | -3.051391600 | 0.000000000 | 0.000000000 |