Supporting Information

A Unified Operator Resolution of Quadratic Bond Orders

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S1 Computational details

The quadratic bond-order analysis and its bond-order-orbital (BOO) resolution are implemented in the Natural Bond-order Analysis (NBA) module of the runEDDB program. The program constructs the natural atomic orbital (NAO) representation internally and reads density matrices from formatted-checkpoint, Molden, ORCA, and other standard wavefunction files. Unless stated otherwise, all bond orders reported in the main text were evaluated in the untruncated NAO basis, so the resolved index corresponds to the full-basis Wiberg–Mayer bond order in the chosen orthonormal atomic representation.

The default runEDDB parameters were used throughout: a quasi-degenerate natural-occupation threshold of 10^{-6} for the occupation-scaled cumulative spectral-layer grouping, an atom-pair gate of 10^{-2} on the bond index, and a BOO printing/export cutoff of 10^{-4}. The gate and cutoff affect only which atom pairs and components are printed or exported. The complete atom-pair eigenbasis is retained internally for the trace-preserving projection, and the reported cumulative channel sums include all retained contributions required to satisfy the corresponding trace relation within numerical precision.

Benzene invariance tests. The ground-state singlet (S_0, D_{6h}) and lowest triplet (T_1, D_{2h}) benzene calculations used Gaussian 16 (rev. C.01) with the def2-QZVPP basis. The closed-shell singlet was evaluated at the RHF, UHF, RMP2, and UMP2 levels, using the same RI-MP2-optimized D_{6h} geometry for the single-point calculations. The lowest triplet was evaluated at the UHF, ROHF, and UMP2 levels. The correlated entries use relaxed MP2 one-particle densities (`Density=MP2`). For the open-shell analyses, the spin-resolved α and β density blocks were used for the per-spin construction, whereas the deliberately naive total-density entries use $\mathbf{P}^{\alpha} + \mathbf{P}^{\beta}$ as a single spin-summed density. The restricted/unrestricted equalities for the closed-shell state were also reproduced in ORCA using the dhf-QZVPP basis.

Main-group and transition-metal clusters. The Li_2Al_4, Li_4Al_4, Ge_4^{2+}, cyclo-P_5^-, $Re_2Cl_8^{2-}$, Hf_3, and Ta_3^- systems were optimized and their densities obtained at the PBEh-3c composite level, i.e., the modified PBE hybrid with the def2-mSVP basis and D3(BJ)+gCP corrections. Closed-shell singlets were treated spin-restricted, whereas the Ta_3^- quintet was treated spin-unrestricted. These calculations provide compact and stable single-reference densities for the channel-resolution tests in the main text.

Actinide systems. The Th_3^q charge series and U_2 were treated with PBE0-D4 and the all-electron scalar-relativistic SARC-DKH-TZVP basis under the second-order Douglas–Kroll–Hess Hamiltonian. For the Th_3^q series, single-point densities were evaluated at the fixed experimental tri-thorium ring geometry, so that only the electron count changes along the charge series. The U_2 septet was evaluated at the literature U–U bond length of 2.43 Å. All cluster calculations used ORCA 6.1.1 with the RIJCOSX approximation and the def2/J or SARC/J Coulomb-fitting basis as appropriate.

The $\sigma/\pi/\delta/\phi$ decomposition reported in the main text should be read as a qualitative channel diagnostic for the stated one-particle densities, not as a benchmark of density functionals or basis sets. The exact trace relation is enforced by the BOO construction itself, whereas the chemical assignment depends on the quality and stability of the underlying density. The compact PBEh-3c basis is useful in this context because it avoids the Rydberg-driven inflation that can affect Mayer-type indices in very diffuse basis sets, while the relativistic PBE0-D4/SARC-DKH treatment provides a consistent scalar-relativistic description of the actinide examples.

S2 Example runEDDB output

The Natural Bond-order Analysis is printed by runEDDB in self-describing blocks. A representative bond-order-orbital output is shown below.

Bond-order orbitals (`-print boo`). The genuine output for the diuranium molecule U_2: the Wiberg bond order is resolved into bond-order orbitals (BOOs), each printed as its occupation (σ^2, summing to the WBO) with a $\sigma/\pi/\delta/\varphi$ symmetry label and the MO range it occupies in the exported wavefunction file. Note the two π and the σ BOOs dominating the U–U multiple bond, with no φ component (the $5f$ φ electrons are non-bonding in the single-determinant density).

```
BOND-ORDER ORBITALS (BOO):

  Unified quadratic bond order resolved into bond-order orbitals (BOOs).
  Each listed component is a BOO occupation with a σ/π/δ/φ symmetry label.
  Only the five largest BOOs above threshold are listed.

     Atom pair          WBO       BOOs         BOO occupations with symmetry labels
  -----------------  --------  ----------  ---------------------------------------------
    1 U   -   2 U     3.2054     1 - 21     0.9975π  0.9973π  0.7344σ  0.2711σ  0.0362σ
  -----------------  --------  ----------  ---------------------------------------------
```

S3 Input files and geometries used

For each system the descriptive line gives the charge, spin multiplicity and the level of theory; the geometry that follows is the one used for the reported density.

S3.1 All-metal and inorganic clusters (PBEh-3c)

Li_4Al_4 (rectangular Al_4^{4-} core, neutral, singlet)

Li4Al4.inp

```
! PBEh-3c TightSCF
* xyz 0 1
  Al    1.29153786    1.25758331    0.00008275
  Al   -1.29132484    1.25691468    0.00016654
  Al   -1.29135738   -1.25855736    0.00000024
  Al    1.29079324   -1.25784251    0.00023105
  Li    0.00017697    0.00157536    2.20102801
  Li    0.00034709    0.00160849   -2.20051683
  Li    3.55212694   -0.00089368    0.00081700
  Li   -3.55229988   -0.00036828    0.00083123
*
```

Li_2Al_4 (square Al_4^{2-} core, neutral, singlet)

Li2Al4.inp

```
! PBEh-3c TightSCF
* xyz 0 1
  Al    1.30109    1.30217    0.00000
  Al   -1.30150    1.30196    0.00000
  Al   -1.30182   -1.30071    0.00000
  Al    1.30118   -1.30069    0.00000
  Li    0.00052   -0.00136    2.27056
  Li    0.00053   -0.00137   -2.27056
*
```

Ge_4^{2+} (square, dication, singlet)

Ge4_2+.inp

```
! PBEh-3c TightSCF
* xyz 2 1
  Ge    1.20198    1.20198    0.00001
  Ge   -1.20198    1.20198   -0.00001
  Ge   -1.20198   -1.20198    0.00001
  Ge    1.20198   -1.20198   -0.00001
*
```

cyclo-P_5^- (planar pentagon, anion, singlet)

P5-.inp

```
! PBEh-3c TightSCF
* xyz -1 1
  P    -0.00000    1.77798    0.00006
  P    -1.69051    0.54916   -0.00001
  P    -1.04465   -1.43816   -0.00005
  P     1.04465   -1.43816    0.00008
  P     1.69051    0.54916   -0.00009
*
```

$Re_2Cl_8^{2-}$ (eclipsed D_{4h}, dianion, singlet; Re–Re $= 2.145$ Å)

Re2Cl8_2-.inp

```
! PBEh-3c TightSCF
* xyz -2 1
  Re   -0.00000   -0.00000    1.07232
  Re   -0.00000    0.00000   -1.07231
  Cl    2.27305   -0.00002    1.66642
  Cl    0.00002    2.27305    1.66642
  Cl   -2.27305    0.00002    1.66642
  Cl   -0.00002   -2.27305    1.66642
  Cl    2.27306    0.00002   -1.66642
  Cl   -0.00002    2.27306   -1.66642
  Cl   -2.27306   -0.00002   -1.66642
  Cl    0.00003   -2.27306   -1.66642
*
```

Hf_3 ($^1A_1'$ equilateral triangle, neutral, singlet; Hf–Hf $= 2.676$ Å)

Hf3.inp

```
! PBEh-3c TightSCF
* xyz 0 1
  Hf    1.54486    0.00019    0.00000
  Hf   -0.77260    1.33804    0.00000
  Hf   -0.77226   -1.33823    0.00000
*
```

Ta_3^- (quintet, near-equilateral; Ta–Ta ≈ 2.46 Å)

Ta3-.inp

```
! PBEh-3c TightSCF
* xyz -1 5
  Ta    1.42037    0.00475    0.00000
  Ta   -0.70607    1.22283    0.00000
  Ta   -0.71430   -1.22758    0.00000
*
```

S3.2 Actinide systems (PBE0/SARC-DKH-TZVP, DKH2)

The Th_3 ring is held at the fixed experimental geometry across the charge series; only the electron count changes.

Th_3^{10+} (2 ring electrons, singlet)

Th3_10+.inp

```
! PBE0 D4 SARC-DKH-TZVP DKH2 RIJCOSX SARC/J defgrid2
* xyz 10 1
  Th    2.30329    0.00000    0.00000
  Th   -1.15164    1.99474    0.00000
  Th   -1.15164   -1.99474    0.00000
*
```

Th_3^{4+} (8 ring electrons, singlet)

Th3_4+.inp

```
! PBE0 D4 SARC-DKH-TZVP DKH2 RIJCOSX SARC/J defgrid2
* xyz 4 1
  Th    2.30329    0.00000    0.00000
  Th   -1.15164    1.99474    0.00000
  Th   -1.15164   -1.99474    0.00000
*
```

Th_3 (neutral, singlet)

Th3_0.inp

```
! PBE0 D4 SARC-DKH-TZVP DKH2 RIJCOSX SARC/J defgrid2
* xyz 0 1
  Th    2.30329    0.00000    0.00000
  Th   -1.15164    1.99474    0.00000
  Th   -1.15164   -1.99474    0.00000
*
```

U_2 (septet, literature bond length 2.43 Å)

U2.inp

```
! PBE0 D4 SARC-DKH-TZVP DKH2 RIJCOSX SARC/J defgrid2
%scf maxiter 500 end
* xyz 0 7
  U    0.00000    0.00000    0.00000
  U    0.00000    0.00000    2.43000
*
```

S4 HPC resources

All calculations were performed using the supercomputer Helios available in the HPC infrastructure PLGrid (ACK Cyfronet AGH, grant no. PLG/2025/018981) and an in-house server with the following specification:

- Model: Supermicro Hyper A+ Server AS-2125HS-TNR.
- Operating system: Debian GNU/Linux x86_64.
- RAM: 24×64 GB DDR5-4800 MHz ECC REG.
- CPU: 2× AMD EPYC 9554 (Genoa), 64C/128T, 3.1 GHz, 256 MB L3.
- NVMe (system): Intel Optane DC P5800X 3.2 TB PCIe 4.0.
- NVMe (scratch): Micron 9400 MAX 12.8 TB PCIe 4.0.
- Network: Supermicro AIOM 2×10 GbE.