

Supporting Information for

On the Linear Geometry of  
Lanthanide Hydroxide ( $\text{Ln—OH}$ ,  $\text{Ln=La-Lu}$ )

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**Table S1.** SCF Energies (in Hartrees) and  $\langle S^2 \rangle$  for the calculated lanthanide hydroxides as reported in the paper.

| Species | SCF Energy (Hartree) | $\langle S^2 \rangle$ |
|---------|----------------------|-----------------------|
| LaOH    | -8563.00300281       | 0.00                  |
| CeOH    | -8929.62359501       | 3.75                  |
| PrOH    | -9305.88197592       | 6.00                  |
| NdOH    | -9691.95412361       | 8.75                  |
| PmOH    | -10087.8561694       | 12.00                 |
| SmOH    | -10493.6827369       | 15.75                 |
| EuOH    | -10909.5568538       | 20.01                 |
| GdOH    | -11335.3692753       | 15.78                 |
| TbOH    | -11771.2721265       | 12.01                 |
| DyOH    | -12217.4110509       | 8.75                  |
| HoOH    | -12673.8254319       | 6.00                  |
| ErOH    | -13140.5508272       | 3.75                  |
| TmOH    | -13617.667165        | 2.00                  |
| YbOH    | -14105.2379132       | 0.75                  |
| LuOH    | -14603.0021252       | 0.00                  |

**Table S2.** Occupations of 4f, 5d, and 6s based non-bonding molecular orbitals of lanthanide hydroxides as described in the paper.

| Species | Orbital occupation                              |
|---------|---|
| LaOH    | 4f <sup>0</sup> 6s <sup>2</sup>                 |
| CeOH    | 4f <sup>1</sup> 6s <sup>1</sup> 5d <sup>1</sup> |
| PrOH    | 4f <sup>2</sup> 6s <sup>1</sup> 5d <sup>1</sup> |
| NdOH    | 4f <sup>3</sup> 6s <sup>1</sup> 5d <sup>1</sup> |
| PmOH    | 4f <sup>4</sup> 6s <sup>1</sup> 5d <sup>1</sup> |
| SmOH    | 4f <sup>6</sup> 6s <sup>1</sup>                 |
| EuOH    | 4f <sup>7</sup> 6s <sup>1</sup>                 |
| GdOH    | 4f <sup>7</sup> 6s <sup>2</sup>                 |
| TbOH    | 4f <sup>9</sup> 6s <sup>1</sup>                 |
| DyOH    | 4f <sup>10</sup> 6s <sup>1</sup>                |
| HoOH    | 4f <sup>11</sup> 6s <sup>1</sup>                |
| ErOH    | 4f <sup>12</sup> 6s <sup>1</sup>                |
| TmOH    | 4f <sup>13</sup> 6s <sup>1</sup>                |
| YbOH    | 4f <sup>14</sup> 6s <sup>1</sup>                |
| LuOH    | 4f <sup>14</sup> 6s <sup>2</sup>                |

As mentioned in the paper, SCF solutions with energies near the reported ground states were located for CeOH, NdOH, and PmOH. Tables S3, S4, and S5 give energies and geometric parameters for the ground state solutions (those reported in the paper) and the nearest energy low-lying state determined during our investigation.

**Table S3.** Electronic configuration, energy, and geometric parameters for low-lying SCF solutions for CeOH.

| Electronic Configuration                        | Energy (eV) | Ce–OH (Å) | CeO–H (Å) | Ce–O–H (°) |
|---|-------------|-----------|-----------|------------|
| 4f <sup>1</sup> 6s <sup>1</sup> 5d <sup>1</sup> | 0.00        | 2.05      | 0.96      | 180.0      |
| 4f <sup>1</sup> 6s <sup>2</sup>                 | 0.18        | 2.06      | 0.95      | 180.0      |

**Table S4.** Electronic configuration, energy, and geometric parameters for low-lying SCF solutions for NdOH.

| Electronic Configuration                        | Energy (eV) | Nd–OH (Å) | NdO–H (Å) | Nd–O–H (°) |
|---|-------------|-----------|-----------|------------|
| 4f <sup>3</sup> 6s <sup>1</sup> 5d <sup>1</sup> | 0.00        | 2.01      | 0.95      | 180.0      |
| 4f <sup>3</sup> 6s <sup>2</sup>                 | 0.03        | 2.07      | 0.95      | 180.0      |

**Table S5.** Electronic configuration, energy, and geometric parameters for low-lying SCF solutions for PmOH.

| Electronic Configuration                        | Energy (eV) | Pm–OH (Å) | PmO–H (Å) | Pm–O–H (°) |
|---|-------------|-----------|-----------|------------|
| 4f <sup>4</sup> 6s <sup>1</sup> 5d <sup>1</sup> | 0.00        | 2.03      | 0.95      | 180.0      |
| 4f <sup>4</sup> 6s <sup>2</sup>                 | 0.04        | 2.03      | 0.95      | 180.0      |

**Table S6.** Comparison of idealized dipole moments of purely ionic LnOH calculated with varied positions of anion charge along the O—H bond.

| Species | Calculated Bond Length | Calculated Dipole Moment (DFT) | Idealized Dipole Moment (Placed at O) | Percent Ionic Character | Idealized Dipole Moment (Placed at H) | Percent Ionic Character | Idealized Dipole moment (Placed halfway b/w O and H) | Percent Ionic Character |
|---------|------------------------|--------------------------------|---------------------------------------|-------------------------|---------------------------------------|-------------------------|--|-------------------------|
| LaOH    | 2.04                   | 0.04                           | 9.76                                  | 0.4                     | 14.36                                 | 0.29                    | 12.06  | 0.35                    |
| CeOH    | 2.05                   | 0.74                           | 9.81                                  | 7.5                     | 14.41                                 | 5.12                    | 12.11  | 6.09                    |
| PrOH    | 2.05                   | 0.87                           | 9.77                                  | 8.9                     | 14.41                                 | 6.02                    | 12.11  | 7.17                    |
| NdOH    | 2.01                   | 1.05                           | 9.62                                  | 10.9                    | 14.22                                 | 7.41                    | 11.92  | 8.84                    |
| PmOH    | 2.03                   | 1.15                           | 9.68                                  | 11.9                    | 14.31                                 | 8.07                    | 12.01  | 9.61                    |
| SmOH    | 2.09                   | 1.24                           | 9.97                                  | 12.4                    | 14.60                                 | 8.49                    | 12.30  | 10.07                   |
| EuOH    | 2.08                   | 1.42                           | 9.95                                  | 14.3                    | 14.55                                 | 9.76                    | 12.25  | 11.60                   |
| GdOH    | 1.96                   | 0.51                           | 9.39                                  | 5.4                     | 13.98                                 | 3.66                    | 11.68  | 4.38                    |
| TbOH    | 2.01                   | 0.60                           | 9.61                                  | 6.2                     | 14.22                                 | 4.20                    | 11.92  | 5.01                    |
| DyOH    | 2.06                   | 1.39                           | 9.82                                  | 14.1                    | 14.46                                 | 9.61                    | 12.16  | 11.42                   |
| HoOH    | 2.05                   | 1.52                           | 9.79                                  | 15.5                    | 14.41                                 | 10.52                   | 12.11  | 12.52                   |
| ErOH    | 2.04                   | 1.51                           | 9.73                                  | 15.5                    | 14.36                                 | 10.48                   | 12.06  | 12.48                   |
| TmOH    | 2.03                   | 1.60                           | 9.69                                  | 16.5                    | 14.31                                 | 11.20                   | 12.01  | 13.34                   |
| YbOH    | 2.02                   | 1.66                           | 9.64                                  | 17.2                    | 14.26                                 | 11.62                   | 11.97  | 13.85                   |
| LuOH    | 1.9                    | 0.47                           | 9.05                                  | 5.2                     | 13.69                                 | 3.46                    | 11.39  | 4.15                    |

Mulliken population analyses for both  $\alpha$  and  $\beta$  molecular orbitals are summarized in Tables S7a and S7b below. It is noteworthy that in several cases the Mulliken analyses exhibit non-zero contributions from lanthanide 4f functions. It is not clear if the participating f-orbitals are simply enhancing variational relaxation and polarization or if they are engaged in bonding in the conventional sense. Determination of the specifics of this matter is beyond the scope of the current paper and we defer such an analysis to the NBO based study described in the paper. Nevertheless, 4f/5d hybridization has been invoked in previous studies of lanthanide compounds, including a recent report by Zhang and co-workers studying PrO<sub>2</sub> (*Scientific Reports* **8**, 15995 (2018)).

The specific interpretation of these Mulliken population analysis results is beyond the scope of the present work. Instead, we rely on the NBO model for the bonding analysis described in the paper. This choice is partially based on the known behavior of Mulliken partitioning. As is well known, Mulliken partitioning can lead to unphysical results particularly when employing basis sets with diffuse functions. In particular, Mulliken analysis can fail to suggest expected electron donation behaviors of ligands. In work on actinide complexes, Clark and co-workers (*J. Chem. Phys.* **121**, 2563 (2004)) showed that the Mulliken model incorrectly predicts that OH<sup>-</sup> is a weaker electron donor than CN<sup>-</sup>. An additional concern raised in Mulliken population analysis, also discussed by Clark and co-workers, is that the definition of bond order does not distinguish between bonding and antibonding interactions which can yield an inaccurate chemical description of the molecules.

**Table 7a. Alpha Mulliken populations of the three bonding molecular orbitals of LnOH**

| Molecule | $\sigma$ Bond   | $\pi$ Bond  | $\pi$ Bond  |
|----------|---|---|---|
| LaOH     | 55.3% O 2p<br>22.0% H 1s<br>8.6% La 6p<br>7.5% La 5d<br>6.3% O 2s               | 92.6% O 2p<br>5.4% La 5d                            | 91.3% O 2p<br>6.2% La 5d                            |
| CeOH     | 57.0% O 2p<br>22.4% H 1s<br>7.1% Ce 5d<br>6.7% O 1s<br>6.5% Ce 6p<br>1.6% Ce 4f | 91.1% O 2p<br>6.2% Ce 5d<br>1.3% H 2p<br>1.1% Ce 4f | 91.0% O 2p<br>6.2% Ce 5d<br>1.3% H 2p<br>1.2% Ce 4f |
| PrOH     | 57.6% O 2p<br>22.7% H 1s<br>6.9% Pr 5d<br>6.7% O 2s<br>5.5% Pr 6p<br>2.1% Pr 4f | 90.1% O 2p<br>6.0% Pr 5d<br>2.5% Pr 4f<br>1.2% H 2p | 90.7% O 2p<br>6.4% Pr 5d<br>1.4% H 2p<br>1.2% Pr4f  |
| NdOH     | 58.4% O 2p<br>23.0% H 1s<br>7.0% O 2s<br>6.1% Nd 5d<br>4.6% Nd 6p<br>2.3% Nd 4f | 89.5% O 2p<br>5.9% Nd 5d<br>2.3% Nd 4f              | 90.6% O 2p<br>6.1% Nd 5d                            |
| PmOH     | 59.7% O 2p<br>23.4% H 1s<br>7.6% O 2s<br>5.3% Pm 6p<br>3.5% Pm 5d               | 90.2% O 2p<br>5.4% Pm 5d                            | 91.0% O 2p<br>5.8% Pm 5d                            |
| SmOH     | 60.0% O 2p<br>23.7% H 1s<br>8.0% O 2s<br>5.1% Sm 5d<br>3.2% Sm 6p               | 91.0% O 2p<br>5.2% Sm 5d                            | 91.2% O 2p<br>5.3% Sm 5d                            |
| EuOH     | 60.2% O 2p<br>24.0% H 1s<br>8.1% O 2s<br>4.9% Eu 5d<br>2.6% Eu 6p               | 89.4% O 2p<br>4.9% Eu 5d<br>3.4% Eu 4f              | 89.4% O 2p<br>4.9% Eu 5d<br>3.4% Eu 4f              |
| GdOH     | 44.0% O 2p<br>32.5% Gd 4f<br>17.8% H 1s   | 89.6% O 2p<br>7.1% Gd 5d                            | 89.6% O 2p<br>7.1% Gd 5d                            |
| TbOH     | 60.3% O 2p<br>24.0% H 1s<br>7.4% O 2s<br>4.7% Tb 4f<br>4.5% Tb 5d               | 84.1% O 2p<br>8.3% Tb 4f<br>5.8% Tb 5d              | 84.1% O 2p<br>8.3% Tb 4f<br>5.8% Tb 5d              |

|      |   |  |  |
|------|---|--|--|
| DyOH | 61.6% O 2p<br>24.5% H 1s<br>8.4% O 2s<br>4.0% Dy 5d<br>2.1% Dy 4f | 58.3% O 2p<br>3.7% Dy 4f<br>2.5% Dy 5d   | 58.3% O 2p<br>3.7% Dy 4f<br>2.5% Dy 5d   |
| HoOH | 62.2% O 2p<br>24.6% H 1s<br>8.6% O 2s<br>3.6% Ho 5d<br>2.2% Ho 4f | 47.8% O 2p<br>48.5% Ho 4f<br>2.63% Ho 5d | 47.8% O 2p<br>48.5% Ho 4f<br>2.63% Ho 5d |
| ErOH | 62.9% O 2p<br>24.8% H 1s<br>8.9% O 2s<br>3.2% Er 5d<br>2.4% Er 4f | 51.7% O 2p<br>44.5% Er 4f<br>2.3% Er 5d  | 66.7% O 2p<br>28.3% Er 4f<br>3.3% Er 5d  |
| TmOH | 63.0% O 2p<br>24.9% H 1s<br>9.0% O 2s<br>3.5% Tm 4f<br>2.7% Tm 5d | 60.0% O 2p<br>36.6% Tm 4f<br>2.3% Tm 5d  | 80.1% O 2p<br>14.0% Tm 4f<br>4.0% Tm 5d  |
| YbOH | 63.7% O 2p<br>25.2% H 1s<br>9.2% O 2s<br>4.0% Yb 4f<br>2.3% Yb 5d | 87.5% O 2p<br>6.5% Yb 4f<br>4.0% Yb 5d   | 87.5% O 2p<br>6.5% Yb 4f<br>4.0% Yb 5d   |
| LuOH | 60.0% O 2p<br>23.3% H 1s<br>6.3% O 2s<br>6.0% Lu 5d               | 90.4% O 2p<br>6.4% Lu 5d                 | 91.4% O 2p<br>6.3% Lu 5d                 |

**Table S7b. Beta Mulliken populations of the three bonding molecular orbitals of LnOH**

| Molecule | $\sigma$ Bond   | $\pi$ Bond               | $\pi$ Bond               |
|----------|---|--------------------------|--------------------------|
| LaOH     | 55.3% O 2p<br>22.0% H 1s<br>8.6% La 6p<br>7.5% La 5d<br>6.3% O 2s | 92.6% O 2p<br>5.4% La 5d | 91.3% O 2p<br>6.2% La 5d |
| CeOH     | 56.8% O 2p<br>22.6% H 1s<br>7.7% Ce 6p<br>6.9% O 2s<br>6.0% Ce 5d | 93.6% O 2p<br>4.4% Ce 5d | 93.5% O 2p<br>4.5% Ce 5d |
| PrOH     | 57.8% O 2p<br>22.8% H 1s<br>7.1% O 2s<br>6.7% Pr 6p<br>5.8% Pr 5d | 93.6% O 2p<br>4.5% Pr 5d | 93.9% O 2p<br>4.2% Pr 5d |
| NdOH     | 58.9% O 2p<br>23.4% H 1s<br>7.5% O 2s<br>6.2% Nd 6p<br>5.3% Nd 5d | 93.8% O 2p<br>4.1% Nd 5d | 93.7% O 2p<br>4.1% Nd 5d |

|      |   |   |   |
|------|---|---|---|
| PmOH | 59.7% O 2p<br>23.4% H 1s<br>8.0% O 2s<br>5.3% Pm 6p<br>4.6% Pm 5d | 93.8% O 2p<br>3.8% Pm 5d                | 94.0% O 2p<br>3.7% Pm 5d                |
| SmOH | 59.2% O 2p<br>23.7% H 1s<br>8.3% O 2s<br>5.4% Sm 6p<br>4.3% Sm 5d | 94.0% O 2p<br>3.7% Sm 5d                | 94.1% O 2p<br>3.5% Sm 5d                |
| EuOH | 59.7% O 2p<br>24.0% H 1s<br>8.5% O 2s<br>4.7% Eu 6p<br>4.1% Eu 5d | 94.1% O 2p<br>3.6% Eu 5d                | 94.1% O 2p<br>3.6% Eu 5d                |
| GdOH | 59.9% O 2p<br>23.9% H 1s<br>6.9% O 2s<br>5.9% Gd 5d               | 92.0% O 2p<br>5.3% Gd 5d                | 92.0% O 2p<br>5.3% Gd 5d                |
| TbOH | 61.3% O 2p<br>24.1% H 1s<br>8.0% O 2s<br>4.6% Tb 5d<br>3.1% Tb 6p | 92.9% O 2p<br>4.5% Tb 5d                | 92.9% O 2p<br>4.5% Tb 5d                |
| DyOH | 61.9% O 2p<br>24.3% H 1s<br>8.7% O 2s<br>3.7% Dy 5d<br>2.4% Dy 6p | 93.4% O 2p<br>3.9% Dy 5d                | 93.4% O 2p<br>3.9% Dy 5d                |
| HoOH | 62.4% O 2p<br>24.5% H 1s<br>8.8% O 2s<br>3.5% Ho 5d               | 92.5% O 2p<br>3.6% Ho 5d                | 92.5% O 2p<br>3.6% Ho 5d                |
| ErOH | 63.1% O 2p<br>24.8% H 1s<br>9.0% O 2s<br>3.1% Er 5d<br>2.0% Er 4f | 90.1% O 2p<br>3.5% Er 5d<br>3.4% Er 4f  | 92.4% O 2p<br>3.6% Er 5d                |
| TmOH | 63.4% O 2p<br>24.9% H 1s<br>9.2% O 2s<br>3.1% Tm 4f<br>2.7% Tm 5d | 73.2% O 2p<br>21.8% Tm 4f<br>2.7% Tm 5d | 71.6% O 2p<br>23.9% Tm 4f<br>2.6% Tm 5d |
| YbOH | 64.1% O 2p<br>25.1% H 1s<br>9.4% O 2s<br>4.1% Yb 4f<br>2.3% Yb 5d | 87.9% O 2p<br>7.0% Yb 4f<br>3.5% Yb 5d  | 87.9% O 2p<br>7.0% Yb 4f<br>3.5% Yb 5d  |
| LuOH | 60.1% O 2p<br>23.2% H 1s<br>6.6% O 2s<br>5.6% Lu 5d               | 92.1% O 2p<br>5.2% Lu 5d                | 93.3% O 2p<br>4.7% Lu 5d                |

### Determination of the effective ionic radii:

Shannon [Acta Cryst. (1976) A32, 751-767] reports the variations in ionic radii in accordance to change in the coordination numbers of ions. While the paper does not provide the ionic radii for singly-coordinated  $\text{Ln}^+$  and  $\text{OH}^-$ , one can estimate it using the available values and their respective trends. In order to provide a proper estimation of the effective ionic radii of  $\text{Ln}^+$ , we consider a possible trend in the ionic radii of 2-coordinated  $\text{M}^+$  versus 6-coordinated  $\text{M}^{3+}$ . For copper and silver, both of those values are reported and, in both cases, the 2-coordinated  $\text{M}^+$  radii are around 85% of the 6-coordinated  $\text{M}^{3+}$ . Starting from this estimation, we scale the reported 6-coordinated  $\text{Ln}^{3+}$  by a factor of 0.85 and the resulting estimated effective ionic radii were used for further bonding analysis.

**Table S8.** Reported effective ionic radii of 6-coordinated  $\text{Ln}^{3+}$  and the estimated  $\text{Ln}^+$  effective ionic radii.

| Species | R 6-coordinated $\text{Ln}^{3+}$ | Estimated 2-coordinate $\text{Ln}^+$ |
|---------|----------------------------------|--------------------------------------|
| LaOH    | 1.03                             | 0.88                                 |
| CeOH    | 1.01                             | 0.86                                 |
| PrOH    | 0.99                             | 0.84                                 |
| NdOH    | 0.98                             | 0.84                                 |
| PmOH    | 0.97                             | 0.82                                 |
| SmOH    | 0.96                             | 0.81                                 |
| EuOH    | 0.95                             | 0.80                                 |
| GdOH    | 0.93                             | 0.79                                 |
| TbOH    | 0.92                             | 0.78                                 |
| DyOH    | 0.91                             | 0.78                                 |
| HoOH    | 0.90                             | 0.77                                 |
| ErOH    | 0.89                             | 0.76                                 |
| TmOH    | 0.88                             | 0.75                                 |
| YbOH    | 0.87                             | 0.74                                 |
| LuOH    | 0.86                             | 0.73                                 |

In a similar approach, and in order to determine an estimate to the effective ionic radius of OH<sup>-</sup>, we explored the relationship between the coordination number and the effective ionic radius of OH<sup>-</sup>. Shannon's reported ionic radii shows a linear relationship between the coordination number and the effective ionic radii. ( $y = 0.012x + 1.3$ ,  $R^2 = 0.969$ ). Using the above equation, we can estimate the effective ionic radius of 1-coordinated OH<sup>-</sup> to be 1.31 Angstroms.

| <b>OH<sup>-</sup></b> | <b>Coordination Number</b> | <b>Effective Ionic Radius</b> |
|-----------------------|----------------------------|-------------------------------|
|                       | 2                          | 1.32                          |
|                       | 3                          | 1.34                          |
|                       | 4                          | 1.35                          |
|                       | 6                          | 1.37                          |