Atomic Ehrenfest forces

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This document collects the supporting figures and table referenced in the main text. Figure S1 shows the z-component of the Hellmann-Feynman force on the H atom in H_2 and on the Li and H atoms in LiH, computed at the FCI level at their experimental bond lengths for the basis sets listed in Table 1 of the main text; it illustrates that the Hellmann-Feynman forces follow the same basis-set trend as the atomic Ehrenfest forces. Figure S2 decomposes the atomic Ehrenfest force into its electron-nuclear, $\mathbf{F}_{en}(\Omega)$, and electron-electron, $\mathbf{F}_{ee}(\Omega)$, contributions for the O atom in H_2O and the Li atom in LiF obtained with the Müller approximation, showing that the dominant basis-set dependence originates in the electron-nuclear term while the electron-electron term also varies appreciably. Table S1 compares the z-component of the atomic Ehrenfest force $\mathbf{F}(\Omega)$ computed with exact orbital representations of the pair density $\rho_2(\mathbf{r}, \mathbf{r}_2)$ against the Müller approximation (values in parentheses) for the same two atoms across the cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis sets, quantifying the close agreement between the two routes. Figure S3 reports the z-component of the Hellmann-Feynman forces on the Li atom in LiF and the O atom in H_2O at the CISD level with varying basis set, and Figure S4 reports the corresponding Hellmann-Feynman forces on the H atom in H_2, the Li atom in LiF and the O atom in H_2O as a function of wavefunction quality (levels of theory listed in Table 2 of the main text), confirming the comparatively weak dependence on the level of theory.

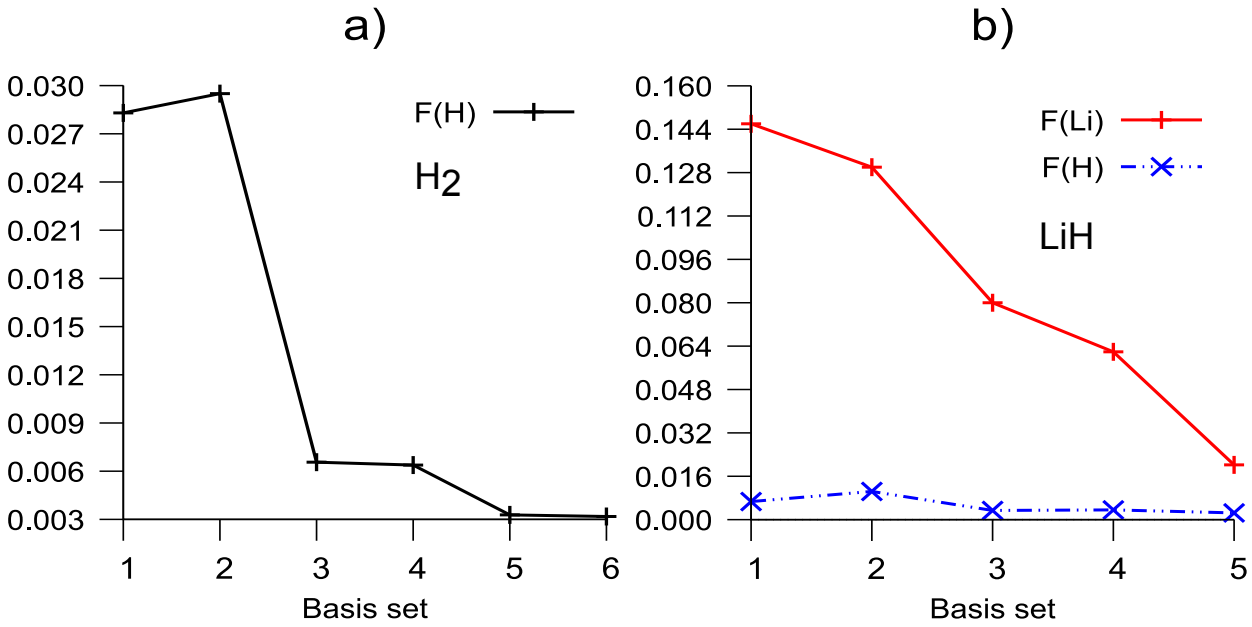


Figure S1: a) Total Hellmann-Feynman force z-component (a.u.) for the left-handed H atom in H_2, as well as b) Li and H atoms in LiH calculated at the FCI level at their corresponding experimental bond lengths, with varying basis sets (IDs shown in Table 1 of the main text).

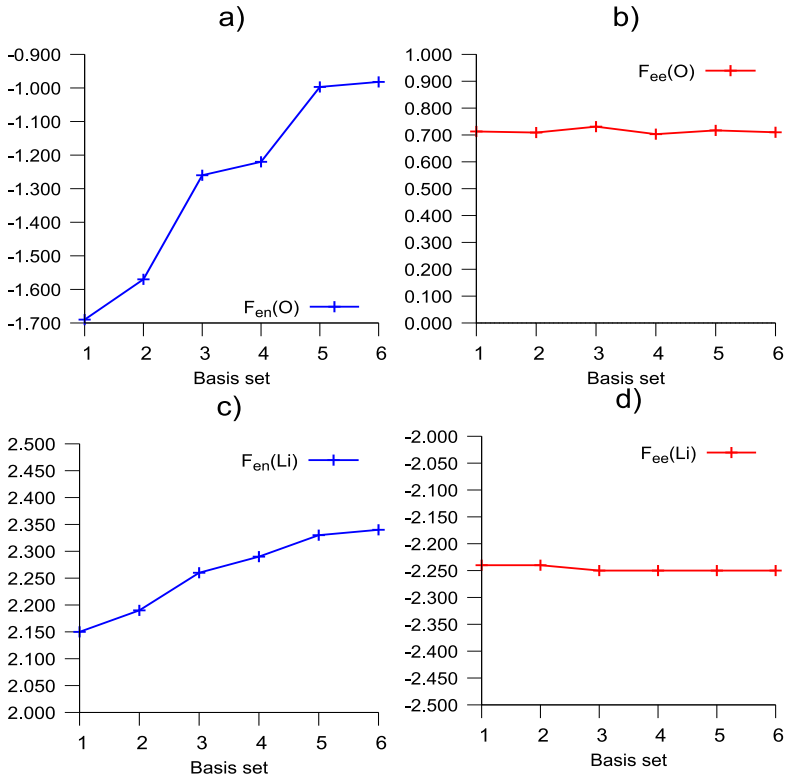
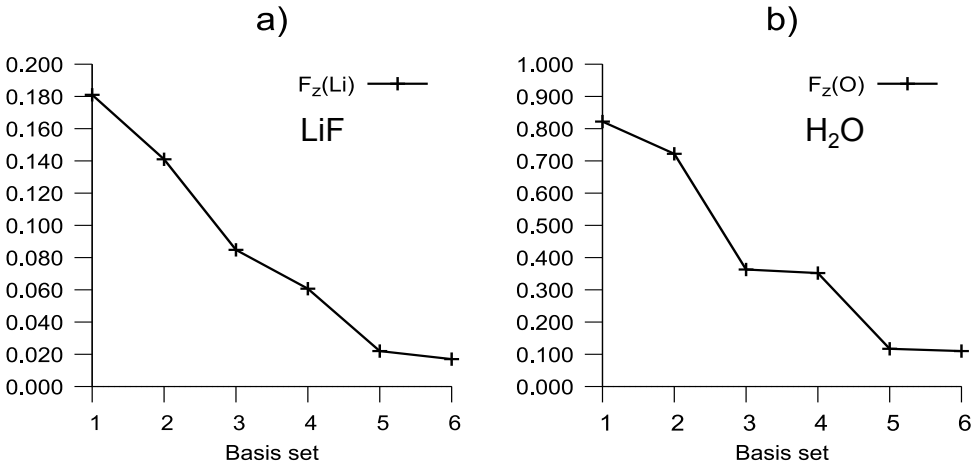


Figure S2: a) and b) show the z-component of $\mathbf{F}_{en}(\Omega)$ and $\mathbf{F}_{ee}(\Omega)$ (a.u.) for the O atom in H_2O using the Müller approximation; c) and d) represent the corresponding values for the Li atom in LiF.

Table S1: Values for the z-component of $\mathbf{F}(\Omega)$ (a.u.) using exact orbital representations of $\rho_2(\mathbf{r}, \mathbf{r}_2)$ for the O atom in H_2O and the Li atom in LiF calculated with the cc-pVDZ (CCD), aug-cc-pVDZ (ACCD), and cc-pVTZ (CCT) basis sets. Values in parentheses denote the corresponding values obtained with the Müller approximation.

Basis/Atom	**CCD**	**ACCD**	**CCT**
O (H_2O)	-0.974 (-0.975)	-0.862 (-0.863)	-0.511 (-0.524)
Li (LiF)	-0.089 (-0.091)	-0.042 (-0.046)	-0.004 (-0.011)

Figure S3: z-component of the Hellmann-Feynman forces (a.u.) for a) the Li atom in LiF and b) the O atom in H_2O at the CISD level with varying basis sets (IDs shown in Table 1 of the main text).



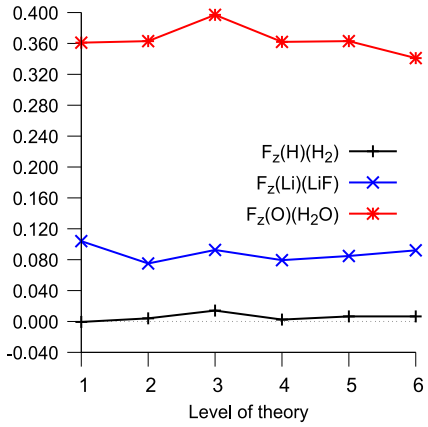


Figure S4: z-component of the Hellmann-Feynman forces (a.u.) for a) the left H atom in H_2, b) the Li atom in LiF and c) the O atom in H_2O with varying wavefunction quality (IDs shown in Table 2 of the main text).