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Atomic Ehrenfest forces

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Abstract

The Ehrenfest force acting on the electrons within an atom of a molecule provides a force-based complement to the energy-centered description of chemical bonding. When integrated over the atomic basins defined by the quantum theory of atoms in molecules, this force can be evaluated either from the divergence of the Pauli kinetic stress tensor or by averaging the electronic force operator over the wavefunction, the latter requiring the pair density. Here we systematically examine how the atomic Ehrenfest force computed by both routes depends on basis-set size and level of theory, using archetypal molecules that represent covalent, polar, ionic, and van der Waals bonding (H_2 , LiH , H_2O , LiF , He_2 , $(\text{NaF})_2$, and CNO^-). We find that the force obtained from the pair density is markedly sensitive to basis-set size, can yield a qualitatively incorrect direction for ionic systems with small basis sets, and converges toward the stress-tensor values as the basis set is enlarged, whereas its dependence on the level of theory is comparatively weak. This behavior parallels that of the Hellmann-Feynman forces and traces to their shared electron-nuclear origin, which also underlies an exact equality between the magnitudes of the total Ehrenfest and Hellmann-Feynman forces.

Keywords: Ehrenfest force, Hellmann-Feynman force, chemical bonding, QTAIM, pair density, basis-set dependence

1 Introduction

Various theoretical frameworks have been developed to quantify the forces governing interatomic interactions, thereby characterizing the complex dynamics exerted on electrons and nuclei within molecular systems. By establishing connections between these fundamental interactions and classical mechanical principles, such models provide a powerful and intuitive framework for describing chemical bonding and molecular architecture. This approach offers a compelling alternative to the traditional energy-centric perspective [1] that has historically dominated chemical theory since the advent of quantum mechanics. Force-based representations ultimately furnish a more tangible and versatile toolkit for predicting chemical phenomena and visualizing the spatial organization of atoms into well-defined molecular structures.

Among the notable conceptions of chemical forces, the Hellmann-Feynman force describes the interactions experienced by nuclei modeled as point charges under the Born-Oppenheimer approximation, derived from the Hellmann-Feynman electrostatic theorem [2]. These forces have served as descriptive and explanatory models for chemically relevant phenomena, including the formation and nature of chemical bonds [3–11] and the modeling of chemical reactions [12–14]. However, a persistent challenge in employing Hellmann-Feynman forces as chemical descriptors alongside conventional electronic structure methods is their marked sensitivity to the electron density, arising as a direct consequence of the Hellmann-Feynman theorem not holding for approximate wavefunctions [15, 16]. Investigations of nuclear forces have prompted several attempts to eliminate the non-physical behavior persisting in these quantities, leading to the development of specialized basis sets designed to mitigate mathematical artifacts stemming from Gaussian basis set incompleteness [17–19]. Nevertheless, no definitive solution has yet been proposed that preserves both their interpretative power and computational efficiency, rendering this an active area of ongoing research.

Conversely, forces acting on electrons can be obtained through the Ehrenfest theorem [20], wherein the Coulombic interactions between these particles yield a net contribution comprising electron-electron repulsions and electron-nuclear attractions. Unlike the Hellmann-Feynman theorem, electrons are treated as a continuous charge distribution rather than point charges. Consequently, selecting a spatially defined region is necessary to compute the average Ehrenfest force via the electronic force operator, $\hat{\mathbf{F}} = -\nabla\hat{V}$. The choice of a physically meaningful spatial domain for defining electron forces depends critically on the explanatory and descriptive objectives for which these forces are intended. In particular, the use of atomic basins defined by the topology of the electron density within the quantum theory of atoms in molecules (QTAIM) [21] has emerged as the de facto standard for obtaining atomic forces in molecular systems. This approach has proven to be a valuable interpretive tool for investigating numerous chemically relevant phenomena related to chemical bonding and molecular structure, with applications including the study of charge redistribution during covalent bond formation [7, 22–24], conformational analysis of alkanes [25], interatomic interactions in organic molecules [26, 27], and other diverse systems [28].

For stationary electronic states, the calculation of atomic Ehrenfest forces typically follows a two-step procedure [21]. First, a force density is defined in real space, yielding the Ehrenfest force field, $\mathbf{F}(\mathbf{r})$. This field is then integrated over an atomic

region (Ω) to determine the net Ehrenfest force on the electrons contained therein, $\mathbf{F}(\Omega)$. $\mathbf{F}(\mathbf{r})$ can be obtained via two distinct approaches: either through the divergence of the Pauli kinetic stress tensor, $\vec{\sigma}(\mathbf{r})$ [21], or by averaging the electronic force operator over the wavefunction [21]. Since the stress tensor is fully determined by the first-order reduced density matrix, the former method has been predominantly employed to date. However, it is well established that $\mathbf{F}(\mathbf{r})$ obtained via the stress tensor exhibits anomalous behavior at large distances from the nuclei [29–33], and a systematic investigation of the implications of these spurious effects on atomic Ehrenfest forces has not, to our knowledge, been reported. Conversely, research into atomic forces using the second approach remains limited, largely due to the scarcity of software capable of calculating Ehrenfest forces in conjunction with QTAIM spatial partitioning, as well as the dependence of these forces on the pair density—a quantity that demands significant computational resources for relatively large molecules and is restricted to wavefunction-based electronic structure methods. In a recent study by the present authors on a small set of molecules [34], it was found that the trend in atomic Ehrenfest forces obtained using the electronic force operator method exhibits a strong dependence on basis set size, following a pattern analogous to that observed for Hellmann-Feynman forces.

On the basis of these considerations, the objective of this work is to conduct a systematic investigation of the behavior of atomic Ehrenfest forces calculated via the two aforementioned methodologies as a function of basis set size and level of theory, employing archetypal molecules representative of different types of chemical bonding. Section 2 presents the general theoretical framework for atomic Ehrenfest forces, Section 3 describes the computational details selected for electronic structure calculations, Section 4 presents the results and their corresponding discussion, and Section 5 displays the conclusions.

2 The Atomic Ehrenfest Force

The starting point for the derivation of the Ehrenfest force density is the electronic force operator, which is defined as the negative gradient of the total Coulomb potential operator $\hat{V}$. This operator encompasses all electrostatic interactions present in the molecular system and can be expressed as:

$$\hat{V} = - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

where the first term accounts for the attractive electron-nuclear interactions and the second term represents the repulsive electron-electron interactions. The indices i and j run over the N electrons, A runs over the M nuclei, Z_A denotes the nuclear charge, and $\mathbf{R}_A$ and $\mathbf{r}_i$ represent the nuclear and electronic coordinates, respectively.

When the electron force operator, $\hat{\mathbf{F}}(\mathbf{r}) = -\nabla\hat{V}$, is averaged over the N -electron wavefunction Ψ , the Ehrenfest force density $\mathbf{F}(\mathbf{r})$ is obtained as shown in Eqn. (2):

$$\begin{aligned}
\mathbf{F}(\mathbf{r}) &= N \int \Psi^* \left(-\nabla_i \hat{V} \right) \Psi d\tau \\
&= -\rho(\mathbf{r}) \sum_{A=1}^M \frac{Z_A(\mathbf{r} - \mathbf{R}_A)}{|\mathbf{r} - \mathbf{R}_A|^3} + \int \frac{\rho_2(\mathbf{r}, \mathbf{r}_2)(\mathbf{r} - \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|^3} d\mathbf{r}_2 \\
\mathbf{F}(\mathbf{r}) &= \mathbf{F}_{\text{en}}(\mathbf{r}) + \mathbf{F}_{\text{ee}}(\mathbf{r})
\end{aligned} \tag{2}$$

The gradient of $\hat{V}$ is taken with respect to any electronic coordinate, as these particles are indistinguishable. The electron-nuclear contribution, $\mathbf{F}_{\text{en}}(\mathbf{r})$, as shown in the first term on the right-hand side of Eqn. (2), depends exclusively on the electron charge distribution, whereas the electron-electron repulsion term $\mathbf{F}_{\text{ee}}(\mathbf{r})$ (second term on the right-hand side of Eqn. (2)) contains the pair density, $\rho_2(\mathbf{r}, \mathbf{r}_2)$, as its fundamental quantity. This can be expressed as the sum of a classical Coulomb contribution and a quantum mechanical exchange-correlation term

$$\rho_2(\mathbf{r}, \mathbf{r}_2) = \rho(\mathbf{r})\rho(\mathbf{r}_2) + \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}_2), \tag{3}$$

where $\rho(\mathbf{r})\rho(\mathbf{r}_2)$ represents the product of one-electron densities, corresponding to the classical contribution, and $\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}_2)$ contains all non-classical effects arising from the antisymmetry of the wavefunction and electron correlation. It can be expressed in its exact form over a finite basis set only for Hartree-Fock and CI-type wavefunctions. For methods that do not provide the pair density explicitly, one may instead resort to reduced density matrix functional theory (RDMFT), which approximates $\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}_2)$ as an explicit functional of the natural orbitals, $\{\phi(\mathbf{r})\}$, and their occupation numbers, $\{n\}$ —the diagonal representation of the first-order reduced density matrix [35]. Writing the pair density as in Eqn. (3), the various natural orbital functionals differ only in the way the latter is reconstructed, generally through a two-index factor $f(n_i, n_j)$ that scales the products of natural orbitals. A number of such functionals have been proposed, including the Buijse-Baerends corrected forms (BBC1 and BBC2) [36], the Csányi-Arias [37] and Goedecker-Csányi-Arias [38] tensor-product expansions, the Goedecker-Umrigar functional [39], the Staroverov-Scuseria functional [40], and the Piris natural orbital functionals (PNOF) [41]. The simplest of these is the Müller approximation [42], which corresponds to the choice $f(n_i, n_j) = (n_i n_j)^{1/2}$ and yields

$$\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}_2) = 2 \sum_{ij} (n_i n_j)^{1/2} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2). \tag{4}$$

We adopt the Müller functional throughout this work, as it has been shown to reproduce the topology of the exchange-correlation Ehrenfest force closely while remaining computationally inexpensive [43]; a systematic assessment of the remaining functionals within the force framework can be found elsewhere [43]. Thus, the electron-electron term of $\mathbf{F}(\mathbf{r})$ can be approximated using Eqn. (4) for methods for which the exact pair density is not available, such as MP2 or DFT.

By virtue of Eqn. (3), $\mathbf{F}_{\text{ee}}(\mathbf{r})$ can be decomposed as

$$\mathbf{F}_{\text{ee}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}_2)(\mathbf{r} - \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|^3} d\mathbf{r}_2 + \int \frac{\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}_2)(\mathbf{r} - \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|^3} d\mathbf{r}_2 \tag{5}$$

$$\mathbf{F}_{ee}(\mathbf{r}) = \mathbf{F}_{\text{Coulomb}}(\mathbf{r}) + \mathbf{F}_{xc}(\mathbf{r}) \quad (6)$$

The Coulomb contribution $\mathbf{F}_{\text{Coulomb}}(\mathbf{r})$ represents the classical electrostatic repulsion between the electron density at position $\mathbf{r}$ and the total electron density distributed throughout space, while the exchange-correlation contribution $\mathbf{F}_{xc}(\mathbf{r})$ accounts for the quantum mechanical effects arising from the Pauli exclusion principle and electron correlation. This latter term has been shown to recover the electronic shell structure and enables the classification of interatomic interactions [44], serving as an emerging tool for describing the nature of bonding through the concept of force, whose chemical information persists even when approximations based on Reduced Density Matrix Functional Theory are employed [43].

$\mathbf{F}(\mathbf{r})$ has proven effective in describing molecular structure [29, 30, 32, 34]. Its topological analysis can identify atomic regions with direct physical interpretation and recover interatomic connectivity consistent with that assigned by chemical rules. The utility of force density fields in studying chemical bonding and molecular structure has become increasingly prominent in the physicochemical literature in recent decades, with various alternative force fields having been proposed that yield valuable chemical insights, thereby providing a solid interpretive foundation for elucidating elusive chemical concepts [45–48].

The Ehrenfest force over the atomic basins defined by QTAIM, $\mathbf{F}(\Omega)$, is calculated by performing a numerical integration of $\mathbf{F}(\mathbf{r})$ defined in Eqn. (2) over such domains in terms of the two corresponding electron-nuclear and electron-electron contributions. The total Ehrenfest force acting on a topological atom Ω thus represents the total attractive force experienced by the electron density contained in this region with all the nuclei of the molecular system plus the repulsive force felt by the electrons within Ω with the remaining electron of the system:

$$\mathbf{F}(\Omega) = \int_{\Omega} \mathbf{F}(\mathbf{r}) d\mathbf{r} = \mathbf{F}_{en}(\Omega) + \mathbf{F}_{ee}(\Omega). \quad (7)$$

Furthermore, as a result of the decomposition introduced in Eqn. (6), the electron-electron contribution to the atomic Ehrenfest force can be similarly separated into its Coulomb and exchange-correlation components:

$$\mathbf{F}_{ee}(\Omega) = \int_{\Omega} \mathbf{F}_{\text{Coulomb}}(\mathbf{r}) d\mathbf{r} + \int_{\Omega} \mathbf{F}_{xc}(\mathbf{r}) d\mathbf{r} = \mathbf{F}_{\text{Coulomb}}(\Omega) + \mathbf{F}_{xc}(\Omega). \quad (8)$$

This decomposition allows for a detailed analysis of the relative importance of classical electrostatic repulsion versus quantum mechanical exchange-correlation effects in determining the net force acting on the electrons within each atomic basin. Such an analysis provides deeper insight into the nature of interatomic interactions and the role of electron correlation in chemical bonding.

Alternatively, according to the hypervirial theorem [49], and due to the hermiticity of the Hamiltonian operator, the expectation value of the Ehrenfest force for the entire molecule, $\mathbf{F}$, is zero

$$\mathbf{F} = N \int \Psi[\hat{H}, \hat{\mathbf{p}}] \Psi d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N = 0, \quad (9)$$

where $\hat{\mathbf{p}}$ represents the linear momentum operator of an electron. Moreover, for a molecule consisting of L topological atoms, $\mathbf{F}$ can be equivalently expressed in terms of the sum of the Ehrenfest force for all of them, as shown in Eqn. (10), where the fulfillment of Eqn. (9) and (10) holds only for exact wavefunctions:

$$\mathbf{F} = \sum_{i=1}^L \mathbf{F}(\Omega_i) = \mathbf{0} \quad (10)$$

The above equation will therefore serve as a reference to assess the behavior of the atomic Ehrenfest forces when both the level of theory and basis set are varied.

3 Computational Details

The atomic Ehrenfest and Hellmann-Feynman forces were calculated for H_2 , LiH , H_2O and LiF with varying basis sets and levels of theory; the results were obtained at their experimental geometries and bond lengths reported in the NIST database <https://cccbdb.nist.gov/>. On the other hand, the dissociation of H_2 and He_2 were studied at the QCISD/cc-pVTZ and MRCI(4,4)/d-aug-cc-pVDZ levels, respectively. Finally, the $(\text{NaF})_2$ and CNO^- systems were analyzed in their corresponding equilibrium geometries obtained at the QCISD/cc-pVTZ level. The electronic structure calculations were performed with Gaussian 16 [50], GAMESS-US [51] and Molpro [52], whereas the Ehrenfest (Müller approximation and stress-tensor) and Hellmann-Feynman forces were computed with AIMall 19 [53], for which the default integration parameters were employed as the program automatically determines the most suitable method for good accuracy in atomic properties. For some cases, the atomic Ehrenfest forces were calculated using the exact orbital representations of $\rho_2(\mathbf{r}, \mathbf{r}_2)$ for correlated wavefunctions with the `promolden` code [54]. Unless otherwise specified, atomic units were employed throughout the work.

4 Results

4.1 H_2 and LiH at the FCI Level

The values of the z -component of $\mathbf{F}(\Omega)$ were calculated for the atoms in H_2 and LiH at the FCI level, using exact representations of $\rho_2(\mathbf{r}, \mathbf{r}_2)$ and the stress-tensor definition, with varying basis set size. The notation selected for each basis set is shown in Table 1.

For H_2 , $\mathbf{F}(\Omega)$ is attractive between both atoms regardless of the basis set, whether calculated via Eqn. (7) or the stress-tensor alternative. As the basis set size increases, the magnitude of $\mathbf{F}(\Omega)$ obtained through Eqn. (7) decreases and converges toward the corresponding values computed from the stress-tensor approach. The fact that $\mathbf{F}(\Omega)$ in both approaches is consistently attractive for both atoms of H_2 is explained by considering the molecular symmetry and the dominant electron-nuclear contribution. The force over Li in LiH exhibits a notable alteration when the basis set size grows from cc-pVDZ to aug-cc-pVTZ, as depicted in Fig. 1b). In the former case, the force over the electrons in this atom is repulsive ($F(\text{Li}) < 0$) and points to the opposite direction from the H atom, as shown in the bottom left panel of Fig. 1. This behavior reverses

when the aug-cc-pVTZ basis set is employed, for which the force exerted over the Li atom becomes attractive ($F(\text{Li}) > 0$) toward the neighboring atom. This phenomenon is not observed when the force is obtained with the stress tensor, for which $\mathbf{F}(\text{Li})$ is always attractive and its behavior remains almost unaffected. Again, as in H_2 , the values and trends of the forces for both atoms converge toward those reported for the stress-tensor approach at the limit of large basis sets. Furthermore, as can be appreciated from Fig. 1d), the sum of $\mathbf{F}(\Omega)$ in LiH approaches zero, reflecting how the quality of the wavefunction improves as one moves toward the infinite basis set limit. The differing basis-set sensitivity of the two routes has a clear origin: the stress-tensor force is determined entirely by the first-order density matrix, whereas the definition involving $\rho_2(\mathbf{r}, \mathbf{r}_2)$ additionally requires an accurate two-particle density and therefore inherits the slower basis-set convergence of the electron-electron distribution. Both formulations coincide in the complete-basis-set limit, where they recover the exact force density of Eqn. (2).

Table 1 Number notation for Dunning’s basis sets employed to calculate the atomic Ehrenfest forces.

Identifier	Basis Set
1	cc-pVDZ
2	aug-cc-pVDZ
3	cc-pVTZ
4	aug-cc-pVTZ
5	cc-pVQZ
6	aug-cc-pVQZ

The tendencies observed in H_2 and LiH for the atomic Ehrenfest forces are parallel to those observed and reported for the Hellmann-Feynman forces, particularly for the electron-nucleus interaction. Fig. S1 of the supplementary information shows the values obtained for the Feynman forces on Li and H nuclei at the computational levels reported above. This statement can be further justified by considering that the Hellmann-Feynman force over the A -th nucleus, $\mathbf{F}_A$, can be expressed as [2]:

$$\mathbf{F}_A = \int \frac{Z_A \rho(\mathbf{r})(\mathbf{r} - \mathbf{R}_A)}{|\mathbf{r} - \mathbf{R}_A|^3} d\mathbf{r} + \sum_{B \neq A}^M \frac{Z_A Z_B (\mathbf{R}_A - \mathbf{R}_B)}{|\mathbf{R}_A - \mathbf{R}_B|^3} \quad (11)$$

As illustrated in Eqn. (2) and Eqn. (11), the same electron-nuclear integral governs both forces (differing only in sign, since one acts on the electrons and the other on the nuclei), thereby representing the source of the anomalous behavior that yields the incorrect nature of the interaction.

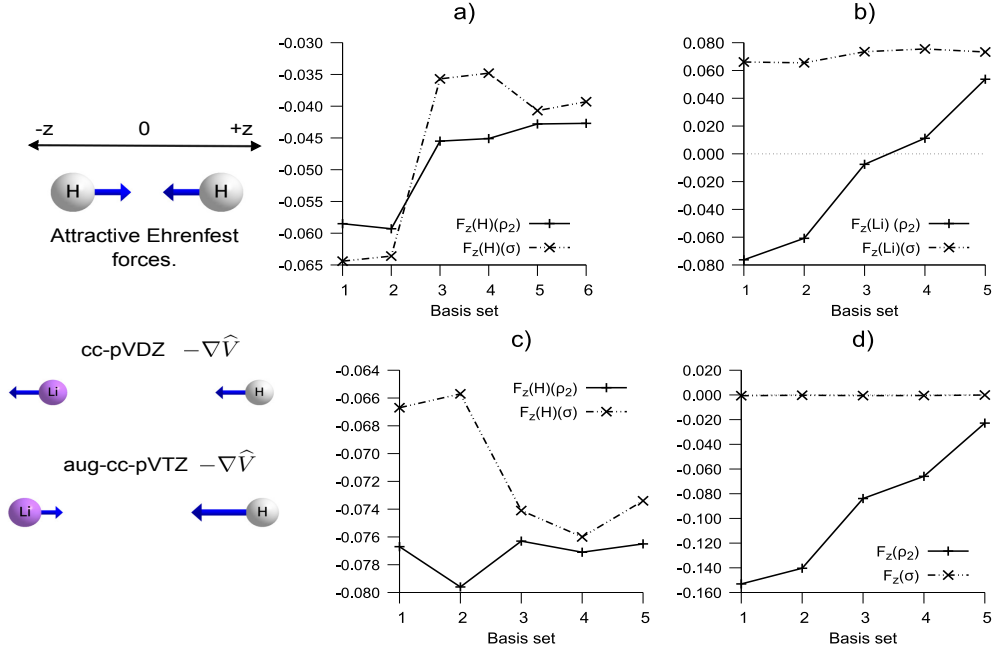


Fig. 1 z -components of $\mathbf{F}(\Omega)$ (a.u.) for a): The right-located H atom of H_2 at the FCI level. b)-c) depict the corresponding forces for the Li and H atoms in LiH, respectively, whereas d) shows the values of $F(\text{Li}) + F(\text{H})$. The molecular models and their orientation in the z -axis are illustrated at the left, where the blue arrows denote the Ehrenfest force vectors.

4.2 H_2O and LiF at the CISD Level Using the Müller Approximation

Figure 2 depicts the z -component of $\mathbf{F}(\Omega)$ for the O atom in H_2O and the Li atom in LiF at their experimental geometries, studied at the CISD level with the basis sets shown in Table 1. In this case, the pair density was approximated in terms of natural orbitals by means of Eqn. (4), whereas the associated orientations of the molecules are indicated in the bottom panels. Again, the Ehrenfest forces in both cases exhibit a notable sensitivity to basis set size when calculated using the definition involving $\rho_2(\mathbf{r}, \mathbf{r}_2)$.

The atomic forces in H_2O are overall attractive toward the neighboring atoms in all cases; the magnitude of the force on the O atom decreases and converges to the force value obtained with the stress-tensor approach at larger basis sets. This tendency is exacerbated for the Li atom in the ionic LiF molecule, where the atomic Ehrenfest force is repulsive when obtained with relatively small basis sets and gradually improves, becoming attractive when triple-zeta quality is employed.

It has been reported for a small number of molecules that $\mathbf{F}(\Omega)$ values obtained using the Müller approximation do not differ significantly from those obtained using exact representations of $\rho_2(\mathbf{r}, \mathbf{r}_2)$ [34]. To ensure that Müller's model allows for the extraction of chemical information and interpretation with a good degree of accuracy

in these systems, the values of $\mathbf{F}(\mathbf{O})$ and $\mathbf{F}(\mathbf{Li})$ for these molecules were obtained and compared for the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ bases using exact forms of $\rho_2(\mathbf{r}, \mathbf{r}_2)$, whose values are shown in Table S1 of the supplementary information. The results show that the values and trends of the atomic Ehrenfest force are quite similar for both methods, which justifies the use of the Müller approximation for the correlated wavefunctions employed in the remaining sections. Additionally, the electron-nuclear and electron-electron contributions of $\mathbf{F}(\Omega)$ for these atoms are depicted in Fig. S2 of the supplementary information, where the significant dependence of $\mathbf{F}(\Omega)$ stems primarily from the electron-nuclear interaction in an analogous way to the case of the Hellmann-Feynman forces, whose z -component for the atoms analyzed are shown in Fig. S3 of the supplementary information. Nonetheless, the electron-electron contribution also changes appreciably with basis set, as can be appreciated in Fig. S2.

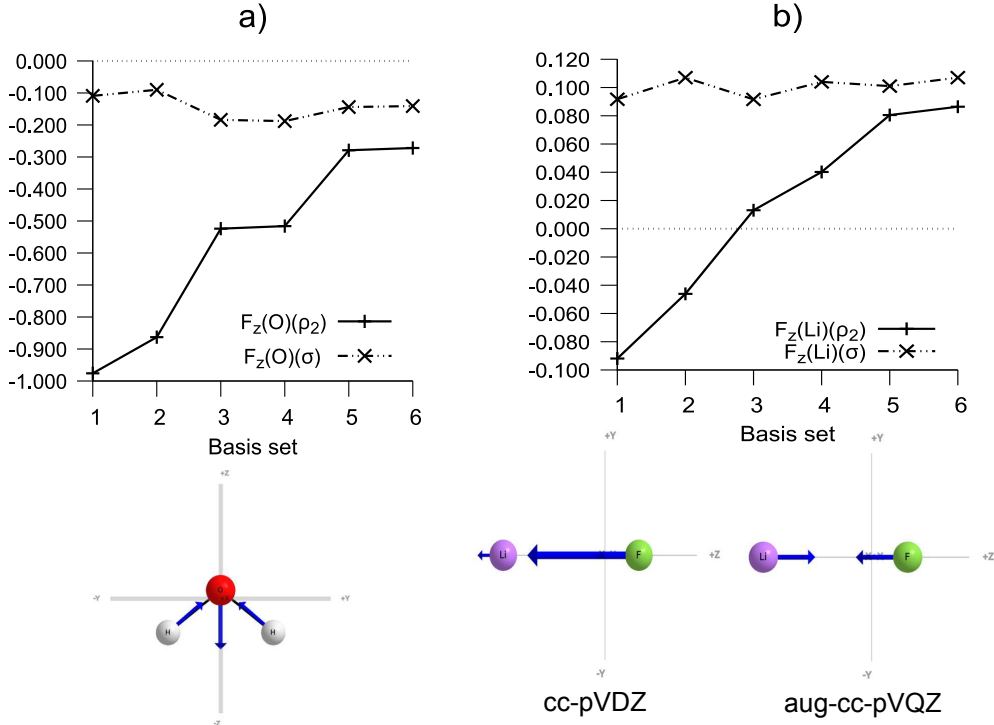


Fig. 2 z -components of $\mathbf{F}(\Omega)$ (a.u.) for a): the O atom in H_2O and b): the Li atom in LiF , both calculated at the CISD level with varying basis set as denoted in Table 1.

4.3 Atomic Forces in the Dissociation of H_2 and He_2

Despite the dependence of atomic Ehrenfest forces on the electronic structure model, it is possible to extract valuable qualitative chemical information that allows for the

interpretation of phenomena of interest, such as the process of chemical bond formation. As an example, Fig. 3a) shows the values of $\mathbf{F}(\Omega)$ and their contributions for the H atom in H_2 located at the left, as a function of internuclear separation; likewise, the values of $\mathbf{F}(\Omega)$ obtained using the stress tensor are shown for comparison.

At large internuclear separations, the atomic Ehrenfest forces are negligible. As the nuclei approach each other, the contribution $\mathbf{F}_{ee}(\mathbf{r})$ begins to dominate $\mathbf{F}_{en}$ as a consequence of the polarization of the electron density of both atoms toward the center of the molecule. This leads to an increase in interelectron repulsion due to the closer proximity of the electrons, which constitutes a preliminary step in the formation of the covalent bond. As the atoms get closer together, the $\mathbf{F}_{en}$ contribution becomes dominant, causing the Ehrenfest forces to become attractive between the nuclei around the equilibrium geometry.

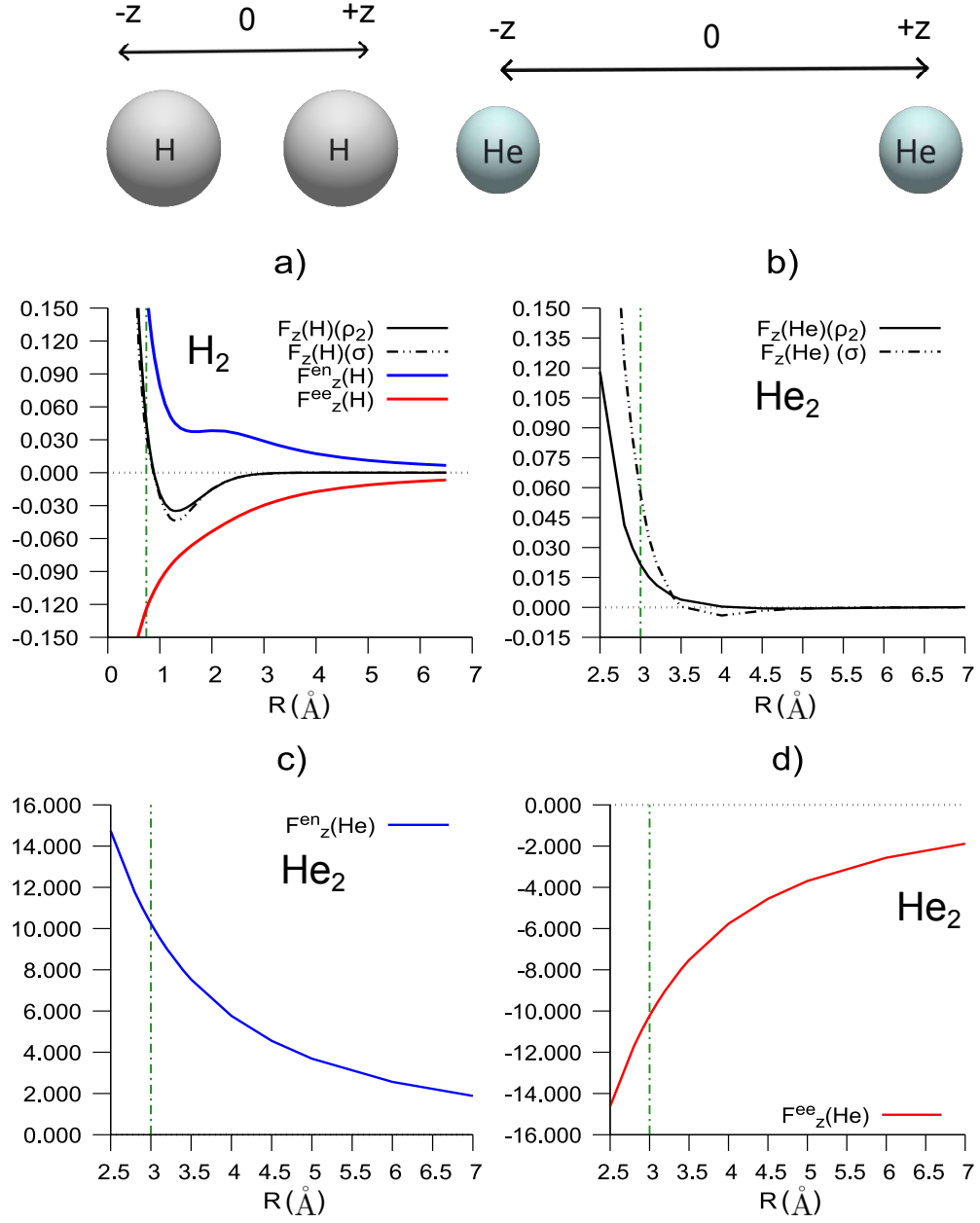


Fig. 3 a) Values of the z -component of $\mathbf{F}(\Omega)$ and its contributions $\mathbf{F}_{en}(\Omega)$ and $\mathbf{F}_{ee}(\Omega)$ (a.u.) for the left-located H atom in H_2 as a function of internuclear separation ($\text{\AA}$). The atomic forces were calculated by means of the Müller approximation at the QCISD/cc-pVTZ level. Panels b), c) and d) depict the corresponding information for the left He atom in He_2 at the MRCI/d-aug-cc-pVDZ level using the exact $\rho_2(\mathbf{r}, \mathbf{r}_2)$. The dashed vertical green lines in a) and b) denote their associated equilibrium separation, in which the Ehrenfest forces between the atoms are attractive.

On the other hand, He_2 is a molecule representative of Van der Waals forces, for which the corresponding $F(\text{He})$ values and its contributions as a function of internuclear separation are also depicted in panels b)-d) of Figure 3, as well as the values obtained with $\vec{\sigma}(\mathbf{r})$. Unlike the behavior exhibited in the case of H_2 , the Ehrenfest force calculated with $\rho_2(\mathbf{r}, \mathbf{r}_2)$ consistently exhibits an attractive behavior, as this arises from the fact that the absence of electron density accumulation in the internuclear region causes the $\mathbf{F}_{en}(\Omega)$ term to dominate over $\mathbf{F}_{ec}(\Omega)$. This tendency has been reported for the integrated Ehrenfest forces in closed-shell interatomic interactions [7].

4.4 Dependence of Ehrenfest Forces on the Level of Theory

The atomic Ehrenfest forces were computed at various levels of theory using fixed geometries and the cc-pVTZ basis set, as shown in Fig. 4 for H_2 , H_2O and LiF molecules. The identifiers for the theory levels used are shown in Table 2.

ID	Level of theory
1	HF (Hartree-Fock)
2	DFT (PBE0)
3	CASSCF
4	MP2
5	CISD
6	FCI/MRCI

Table 2 IDs for the levels of theory employed to calculate the atomic Ehrenfest forces. In all cases cc-pVTZ basis set and the Müller approximation of $\rho_2(\mathbf{r}, \mathbf{r}_2)$ was used. Only for H_2 a FCI calculation could be performed.

In contrast to the basis set size, the level of theory has a considerably smaller influence on the sensitivity of atomic Ehrenfest forces. This observation can be rationalized by the same arguments invoked for the Hellmann–Feynman forces, where the description of the electron density near the nuclei — governed primarily by the basis set quality — plays a more decisive role than either the level of theory or the inclusion of electron correlation [19]. Indeed, the electron–nuclear contribution is strongly dependent on the cusp condition that the electron density must fulfil at the nuclear positions, a condition that is not satisfied when using an incomplete Gaussian-type basis set. Consistent with this, the behavior of $\mathbf{F}(\Omega)$ as a function of the level of theory closely parallels that of the Hellmann–Feynman forces, which were computed for the same molecules at the levels of theory listed in Table 2; the corresponding z-components of the Feynman forces are displayed in Fig. S4 of the supplementary information.

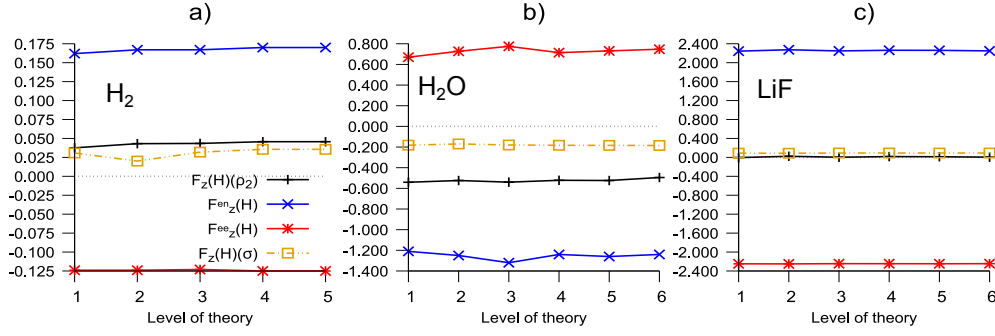


Fig. 4 z-component of $\mathbf{F}(\Omega)$ and its contributions (a.u.) calculated for different levels of theory at a fixed cc-pVTZ basis set for a) The left H atom in H_2 , the O atom in H_2O and the Li atom in LiF . The yellow dashed lines denote the $\mathbf{F}(\Omega)$ obtained with the stress-tensor.

4.5 Atomic Ehrenfest Forces in Other Polyatomic Molecules

In general, the behavior of atomic Ehrenfest forces is qualitatively incorrect for ionic molecules when relatively small basis sets are used. Although it may happen that the sum of the forces of all atoms is zero due to symmetry considerations, this does not guarantee that the description of these interactions is correct. As an example, the $\mathbf{F}(\Omega)$ vectors for the Na and F atoms in the $(\text{NaF})_2$ dimer, as well as for the C, N, and O atoms in the CNO^- anion, are shown in Fig. 5. For $(\text{NaF})_2$, the Ehrenfest forces acting on the Na atoms are repulsive and directed outward from the molecular system, while the forces acting on the fluorine atoms are attractive. In contrast, all force vectors obtained from the stress tensor are directed toward the center, and Eqn. (10) is fulfilled in both scenarios owing to the high symmetry of the molecules. For the CNO^- anion, the two approaches yield Ehrenfest forces with similar trends, although only the stress-tensor results satisfy the sum rule (i.e., the forces sum to zero).

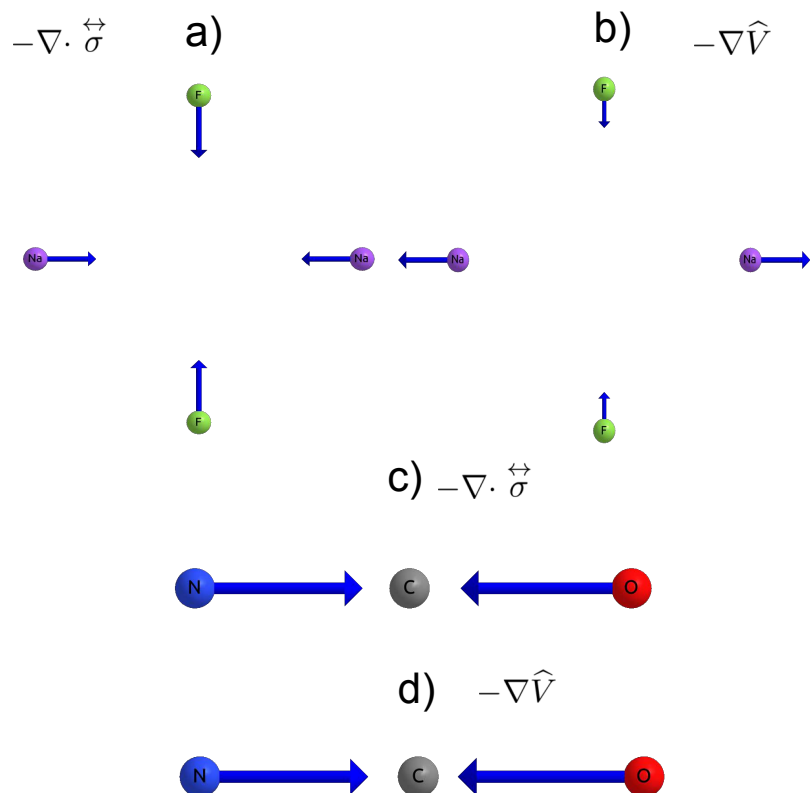


Fig. 5 a) and b) depicts the atomic Ehrenfest force vectors for Na and F atoms using the stress-tensor and the definition involving $\rho_2(\mathbf{r}, \mathbf{r}_2)$, respectively. c) and d) depict the same information for atoms in CNO^- , where the net force on the C atom is negligible. Both molecules are optimized at their corresponding equilibrium geometries determined at the QCISD/cc-pVTZ level; the forces were calculated by means of the Müller approximation.

4.6 Comparison between the magnitudes of the Ehrenfest and Hellmann-Feynman forces

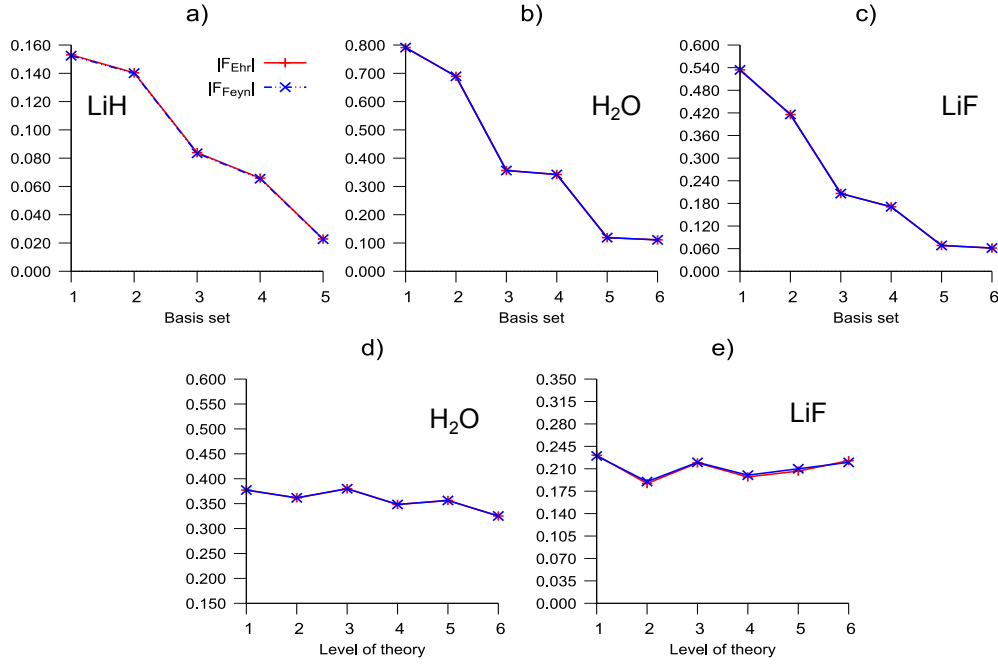


Fig. 6 The magnitudes of $|\mathbf{F}_{Ehr}|$ and $|\mathbf{F}_{Feyn}|$ (a.u.) are shown in panels (a)–(c) for LiH (FCI), H₂O (CISD), and LiF (CISD), respectively, as a function of the basis set. Panels (d) and (e) display the corresponding magnitudes for H₂O and LiF at various levels of theory, with the corresponding method identifiers given in Table 2.

In order to provide a more explicit comparison between the atomic Ehrenfest and Hellmann-Feynman forces, the magnitude of each for the whole molecular system was calculated for molecules in which the charge distribution is asymmetric among the atoms. The magnitude of the total Ehrenfest force acting on the molecule, denoted as $|\mathbf{F}_{Ehr}|$, is computed as the norm of the vector sum of the Ehrenfest forces over all K topological atoms (Ω):

$$|\mathbf{F}_{Ehr}| = \sqrt{\left(\sum_{i=1}^K F_x\right)^2 + \left(\sum_{i=1}^K F_y\right)^2 + \left(\sum_{i=1}^K F_z\right)^2} = \left|\sum_{i=1}^K \mathbf{F}(\Omega_i)\right| \quad (12)$$

The same expression applies to the magnitude of the total Hellmann-Feynman force, $|\mathbf{F}_{Feyn}|$. As mentioned above, for a stationary state described by an exact wavefunction, one has $|\mathbf{F}_{Ehr}| = 0$, whereas for a molecule in its equilibrium geometry, $|\mathbf{F}_{Feyn}| = 0$. Such quantities were calculated for LiH, H₂O, and LiF with varying basis

sets in LiH and varying basis sets and levels of theory in H₂O and LiF. The results are shown in Fig. 6. In all cases, the magnitudes of both quantities tend to zero as the basis set limit tends to infinity, reflecting how the ability of the wavefunction to satisfy the Ehrenfest and Hellmann-Feynman theorems improves accordingly. Since the calculations were carried out at the experimental geometries rather than at the stationary point of each individual method and basis set combination, the residual magnitudes reported here reflect both the incompleteness of the wavefunction and the small offset between the experimental and computed equilibrium geometries. In all the examples analyzed, the two magnitudes were found to coincide, $|\mathbf{F}_{Ehr}| = |\mathbf{F}_{Feyn}|$. As anticipated from Newton’s third law, this equality is in fact an exact identity that holds for any electron density and molecular geometry, and follows directly from the structure of the two forces. Summing the Ehrenfest force over all topological atoms is equivalent to integrating $\mathbf{F}(\mathbf{r})$ over the whole space, so that the electron-electron contribution becomes

$$\sum_{k=1}^K \mathbf{F}_{ee}(\Omega_k) = \iint \frac{\rho_2(\mathbf{r}, \mathbf{r}_2)(\mathbf{r} - \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|^3} d\mathbf{r} d\mathbf{r}_2 = \mathbf{0}, \quad (13)$$

which vanishes identically because the pair density $\rho_2(\mathbf{r}, \mathbf{r}_2)$ is symmetric under the exchange $\mathbf{r} \leftrightarrow \mathbf{r}_2$ while the vector kernel $(\mathbf{r} - \mathbf{r}_2)/|\mathbf{r} - \mathbf{r}_2|^3$ is antisymmetric. Consequently, the total Ehrenfest force reduces to its electron-nuclear part, $\sum_k \mathbf{F}(\Omega_k) = \sum_k \mathbf{F}_{en}(\Omega_k)$. By the same argument, summing the Hellmann-Feynman force of Eqn. (11) over all nuclei annihilates the nuclear-nuclear repulsion term, since $Z_A Z_B (\mathbf{R}_A - \mathbf{R}_B)/|\mathbf{R}_A - \mathbf{R}_B|^3$ is antisymmetric in $A \leftrightarrow B$, leaving only the electron-nuclear term $\sum_A Z_A \int \rho(\mathbf{r})(\mathbf{r} - \mathbf{R}_A)/|\mathbf{r} - \mathbf{R}_A|^3 d\mathbf{r}$. The total Ehrenfest force reduces to the same integral with the opposite sign, since it describes the force exerted on the electrons rather than on the nuclei. Both totals therefore differ only in sign, $\mathbf{F}_{Ehr} = -\mathbf{F}_{Feyn}$ as vectors, as required by Newton’s third law, and hence $|\mathbf{F}_{Ehr}| = |\mathbf{F}_{Feyn}|$ regardless of the level of theory, basis set, or geometry. This shared electron-nuclear origin also explains why both forces exhibit the same pronounced sensitivity to basis-set incompleteness discussed throughout this work.

5 Conclusions

We have carried out a systematic study of the atomic Ehrenfest force $\mathbf{F}(\Omega)$ computed over QTAIM basins as a function of basis-set size and level of theory, comparing the two available routes—the electronic force operator acting on the pair density (in its exact and Müller-approximated forms) and the divergence of the Pauli kinetic stress tensor—for a set of molecules representative of covalent (H₂), polar (H₂O), ionic (LiH, LiF, (NaF)₂), and van der Waals (He₂) interactions, together with the CNO[−] anion.

The atomic Ehrenfest force obtained from the pair density is strongly sensitive to the size of the basis set. For the ionic systems, this sensitivity is severe enough to reverse the direction of the force: with small basis sets $\mathbf{F}(\Omega)$ on the electropositive atom is spuriously repulsive and points away from its bonding partner, and only becomes

attractive, recovering the physically expected behavior, as the basis set reaches triple-zeta quality and beyond. As the basis set is enlarged, both the values and the trends converge toward those of the stress-tensor route, which is comparatively insensitive to basis-set incompleteness because it depends solely on the first-order density matrix. In contrast, the dependence of $\mathbf{F}(\Omega)$ on the level of theory, and hence on the treatment of electron correlation, is much weaker.

This behavior mirrors that long documented for the Hellmann-Feynman forces and originates in the electron-nuclear contribution shared by both quantities, which is acutely sensitive to the description of the electron density near the nuclei—a region governed by the nuclear cusp condition that Gaussian basis sets satisfy only imperfectly. The Müller approximation was found to reproduce the exact pair-density results closely, confirming that it retains the chemically relevant information at a much reduced computational cost. Finally, we showed that the magnitudes of the total Ehrenfest and Hellmann-Feynman forces are exactly equal for any density and geometry, a consequence of the electron-electron and nuclear-nuclear terms vanishing by antisymmetry so that both totals reduce to the same electron-nuclear integral.

Taken together, these results indicate that, while the atomic Ehrenfest force is a valuable descriptor of interatomic interactions, care must be taken when interpreting it from pair-density calculations with modest basis sets, particularly for ionic systems where the vanishing of the summed force imposed by symmetry can mask a qualitatively incorrect description of the individual atomic forces. Adequately flexible, augmented basis sets are required for the pair-density route to yield reliable chemical conclusions.

Supplementary information. Supplementary information accompanies this paper as a separate document (`si.tex`). It contains a descriptive summary together with four supporting figures (Figs. S1–S4) and one table (Table S1): the Hellmann-Feynman forces on the nuclei of H_2 and LiH at the FCI level with varying basis set (Fig. S1); the electron-nuclear and electron-electron decomposition of the atomic Ehrenfest force for the O atom in H_2O and the Li atom in LiF (Fig. S2); a comparison of the exact-pair-density and Müller-approximated atomic Ehrenfest forces for those two atoms (Table S1); and the Hellmann-Feynman forces on the same atoms as a function of basis set (Fig. S3) and level of theory (Fig. S4).

Declarations

Competing interests. The authors declare no competing interests.

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Data availability. The data supporting this work are contained in the manuscript and the Supporting Information, as well as available from the corresponding author upon reasonable request.

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