

## Quantifying the Role of Orbital Contraction in Chemical Bonding

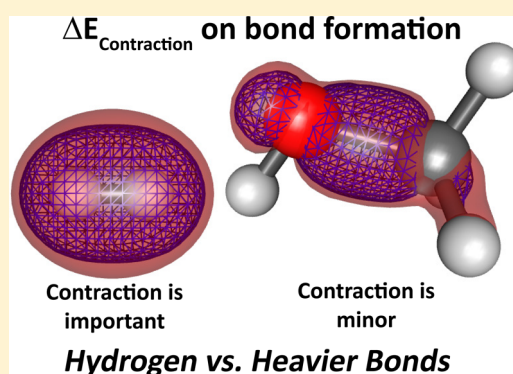
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## Supporting Information

**ABSTRACT:** This work reports an approach to variationally quantify orbital contraction in chemical bonds by an extension of an energy decomposition analysis (EDA). The orbital contraction energy is defined as the energy lowering due to optimization of the isolated fragments (that combine to form the bond) with a specially constructed virtual set of contraction/expansion functions. This set contains one function per occupied orbital, obtained as the linear response to scaling the nuclear charges. EDA results for a variety of single bonds show substantial changes in the importance of orbital contraction; it plays a critical role for bonds to H but only a very minor role in the bonds between heavier elements. Additionally, energetic stabilization due to rehybridization is separated from inductive polarization by the fact that no mixing with virtual orbitals is involved and is shown to be significant in fragments such as  $\text{NH}_2$ , OH, and F.



The physical origin of the covalent bond was the topic of vigorous debate in the 20th century. At the core, the two main positions disagreed on whether bond formation was driven by potential energy<sup>1</sup> or kinetic energy<sup>2</sup> stabilization. Proponents of potential-driven bond formation pointed to the accumulation of electron density in the internuclear region and arguments based on the virial theorem.<sup>1,3,4</sup> Arguments for kinetic-driven bond formation were based around the fact that covalent bonding could only be accounted for in a quantum mechanical treatment, while a classical treatment, which would capture the potential energy effects, cannot.<sup>5</sup> Ultimately, for  $\text{H}_2^+$  and  $\text{H}_2$ , the kinetic-driven interpretation was proven to be correct by explicitly calculating the kinetic and potential energy along the bond formation coordinate by Ruedenberg,<sup>6,7</sup> Goddard,<sup>8</sup> Kutzelnigg,<sup>8,9</sup> and Bacskay and Nordholm<sup>10,11</sup> (although some<sup>12</sup> still argue for potential-driven mechanisms).

Very early work<sup>13</sup> suggested that orbital contraction was also important in accounting for the binding energy of  $\text{H}_2$ . As part of his classic analysis of the  $\text{H}_2^+$  chemical bond,<sup>5</sup> Ruedenberg emphasized that the apparent violation of the virial theorem is resolved by a lowering of the atomic potential via orbital contraction toward the nuclei. For  $\text{H}_2^+$ , at  $R = 2a_0$ , variational calculations show that 1s orbital contraction (from exponent  $\alpha = 1$  to  $\alpha = 1.24$ ) accounts for 21 kcal/mol out of the 64 kcal/mol of chemical binding.<sup>11,14</sup> Other studies by Ruedenberg<sup>6,15–19</sup> and Kutzelnigg<sup>8,9</sup> showed that, for many molecules, orbital contraction is the dominant change in the electron potential energy term on bond formation. Constrained variational calculations for molecules in small basis sets<sup>20,21</sup> suggested that orbital contraction could typically be responsible for 25% or more of the chemical binding energy.

Our objective in this paper is to introduce a variational approach to the orbital contraction contribution to chemical binding as part of an energy decomposition analysis (EDA) of chemical bonds. In an EDA, the energetic contributions of different physical phenomena are computed by some means, such as a sequence of variational constraints. There is a wide range of successful EDA approaches.<sup>22–28</sup> We focus here on the EDA based on the use of Absolutely Localized Molecular Orbitals (ALMOs), which has been used to understand the nature of a variety of noncovalent interactions,<sup>29–35</sup> radical–neutral interactions,<sup>36,37</sup> and covalently bonded interactions.<sup>38</sup> In this approach, the system of interest is broken into a number of interacting fragments. These fragments are allowed to relax to a supersystem ground state via a sequence of variational constrained optimizations where successive constraints are designed to correspond to different physical processes. The A–B single bond energy in a two electrons in two orbitals (AB and  $\text{AB}^*$ ) complete active space (CAS) is variationally decomposed as<sup>38</sup>

$$\Delta E_{\text{interaction}} = \Delta E_{\text{GEOM}} + \Delta E_{\text{FRZ}} + \Delta E_{\text{SC}} + \Delta E_{\text{POL}} + \Delta E_{\text{CT}} \quad (1)$$

Evaluation of the A–B interaction starts by calculating the geometric distortion energy,  $\Delta E_{\text{GEOM}}$ , the energetic cost of changing from optimal fragment geometries for A and B to their geometries in the A–B system. The ALMO EDA computes the MOs of each fragment in isolation. Keeping

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those orbitals fixed (“frozen”), they are brought together to form a (nonorthogonal) supersystem whose molecular orbital matrix is block-diagonal (that is, each orbital is “absolutely localized” to a given fragment). The energy change,  $\Delta E_{\text{FRZ}}$ , from bringing these fragments together is identified as frozen interactions which consist of electrostatics, Pauli repulsion, and dispersion. In the case of a bonded interaction, the assembled supersystem is high-spin, and so a spin-flip is carried out to form the low-spin CSF of the supersystem. This spin-flip stabilization energy,  $\Delta E_{\text{SC}}$ , is termed the spin-coupling energy and reflects covalent bond formation with the frozen orbitals, and is the term most related to the kinetic energy stabilization on bond formation. The assembled supersystem is then optimized by self-consistent field for molecular interactions (SCFMI),<sup>29,36</sup> which allows only on-fragment mixing of frozen occupied MOs with carefully selected fragment virtual orbitals that describe electrical polarization.<sup>37</sup> The energy lowering due to this optimization,  $\Delta E_{\text{POL}}$ , is identified with on-fragment polarization because, in a Mulliken sense, no charge has been transferred between the fragments. Removing the ALMO constraint and permitting all orbital rotations affords the final SCF solution; this energy lowering,  $\Delta E_{\text{CT}}$ , is described as charge transfer because electrons can move between fragments and on-fragment electronic changes (to first order) have already been accounted for by the polarization step.

Energy lowering due to orbital contraction is not specifically identified in the terms of eq 1, so which term does it stabilize in the above scheme? To have a useful basis set limit,<sup>39,40</sup> polarization in the bonded ALMO-EDA involves on-fragment mixing of the occupied frozen MOs with just a small set of virtual MOs, which are the fragment electric response functions (FERFs) that exactly describe linear response to electric fields and field gradients.<sup>37</sup> By design, these FERFs describe electrical polarization; that is, FERFs can describe on-fragment electronic changes that are induced by electric fields due to the other fragment(s). For an example of what the FERFs are like, we note that the dipolar response of the H atom to a uniform field is a p function in the direction of the field, while the quadrupolar responses to field gradients are a set of d functions. By contrast, the orbital contraction that takes place during bond formation is not associated with any change in multipole moment of the fragments (for instance, the 1s orbital of the H atom becomes smaller upon H–H bond formation). Thus the FERFs will not effectively capture orbital contraction effects, which therefore reside primarily in the CT term. Orbital contraction is a CT effect, but one which is intrafragment (even intra-atomic) rather than interfragment.

To begin our explorations of the magnitude of orbital contraction, we generated ALMO EDA data on the covalent bond in H<sub>2</sub> (these and all other calculations were performed with the Q-Chem software package<sup>41</sup>). In the aug-cc-pV5Z basis set,<sup>42</sup> the FERF polarization stabilization is only 2.0 kcal/mol. If we instead permit on-fragment mixing between the frozen occupied orbitals and *all* virtuals of that fragment (this is the original ALMO polarization model), then polarization is 28.6 kcal/mol. The total POL+CT (which is constant regardless of polarization method) is 29.4 kcal/mol. In other words, in the FERF polarization model, nearly all of the stabilization is attributed to CT, while in the ALMO polarization model, nearly all of the stabilization is polarization. Of course, in the large quintuple zeta basis set, it is known that the ALMO polarization will grow to engulf the CT term.<sup>39,40</sup> Hence, it must be checked whether the polarization allowed by

the ALMO but not by the FERF method is really the orbital contraction contribution or an artifact of an overcomplete basis set.

We truncate the aug-cc-pV5Z basis so that it contains only s-type functions. By use of a basis of only s functions, the FERF polarization is necessarily 0 (the response of an s function to an electric field is always a higher angular momentum function). In this basis, ALMO polarization remains 21.3 kcal/mol of 27.2 kcal/mol total POL+CT. We note in passing that the reduction of 2.2 kcal/mol in POL+CT due to removing all functions with  $l > 0$  agrees very well with the FERF estimate of 2.0 kcal/mol for POL. Removing the most diffuse s function as well (which would cut down on any spurious CT-absorbing effects) gives the same result: 21.3 kcal/mol of 27.2 kcal/mol total. Removing the next most diffuse function gives a similar 17.9 out of 24.1 kcal/mol. We can therefore conclude that orbital contraction accounts for ~21 kcal/mol in the H<sub>2</sub> bond. We applied this same analysis to Li<sub>2</sub>, LiH, and BeH and found that the value of this orbital contraction is 0.6, 3.2, and 11.3 kcal/mol, respectively. This straightforward approach cannot, however, be readily extended to systems where the bonds involve heavier elements with partially occupied p shells.

Instead, we seek a generalization of the FERF procedure that augments the previously described FERF virtual space with additional functions that describe orbital contraction. In the spirit of FERFs, in which the appropriate virtual space is determined as a response to a finite electric-field perturbation, the appropriate contraction FERFs are determined as the orbitals required to respond to a perturbation of the nuclear charge. For an atom, this corresponds to the addition of a small electric monopole, located at the nucleus, which gives rise to a monopole FERF effect. For a molecular fragment, scaling the nuclear charge of all nuclei allows the electron density to contract toward all atomic centers (and, as long as the number of occupied orbitals is greater than the number of atoms, which is almost always the case, the resulting FERFs may be localized to each atomic center separately, preserving the atomic-like picture; see the [Supporting Information](#)). These functions may be determined in an identical manner as the original FERF scheme and introduce one new virtual function for each occupied orbital. With superscripts as derivatives,  $\Delta$  is an orbital perturbation,  $Z$  is a nuclear charge perturbation,  $V_{\text{NE}}$  is the nuclear-electron attraction, and  $P$  is the density, then the monopole FERFs may be solved by the coupled perturbed-SCF linear equation

$$E^{\Delta\Delta} \cdot \Delta^Z = -E^{\Delta Z} = -V_{\text{NE}}^Z \cdot P^{\Delta} \quad (2)$$

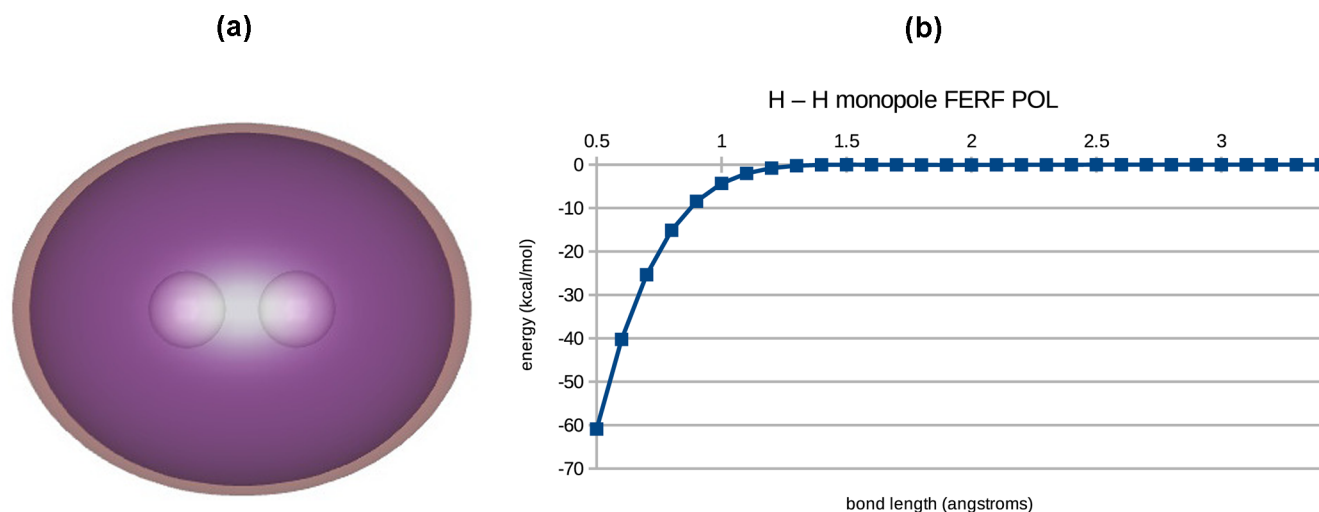
Then,  $V_{\text{NE}}^Z$  is just the  $V_{\text{NE}}$  term with all unit nuclear charges.

$$V_{\text{NE}} = \sum_{\alpha} Z_{\alpha} \int \frac{\phi_{\mu}(r) \phi_{\nu}(r)}{|r - A_{\alpha}|} dr \quad (3)$$

$$V_{\text{NE}}^Z = \sum_{\alpha} \int \frac{\phi_{\mu}(r) \phi_{\nu}(r)}{|r - A_{\alpha}|} dr \quad (4)$$

Inclusion of the monopole FERFs therefore adds one additional right-hand side vector to the FERF linear problem per occupied orbital, which may be solved simultaneously with the other FERFs by conjugate gradients.

We compute the polarization in H<sub>2</sub> using monopole FERFs and find a new polarization energy of 20.9 kcal/mol, closely matching what was calculated in the basis of only s functions.



**Figure 1.** (a) Polarized  $H_2$  densities with MDQ FERFs (purple) and DQ FERFs (red) at an isovalue of 0.02. Note that the addition of monopole FERFs permits orbital contraction. (b) Monopole FERF POL for  $H_2$ . Note that the monopole FERF POL energy is  $<1$  kcal/mol by the time the bond is stretched from 0.8 to 1.2 Å.

The  $H_2$ -polarized densities employing DQ (i.e., standard FERFs) and MDQ FERFs are shown in Figure 1a and confirm that the effect of the introduction of monopole FERFs is to allow orbital contraction. Moreover, computations of the monopole FERF polarization for  $H_2$  over the whole potential energy surface in aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pVSZ basis sets are within 1 kJ/mol of each other, verifying a nontrivial basis set limit. The addition of monopole FERFs does not affect the energy in the nonoverlapping regime (see Figure 1b), and thus the asymptotic behaviors of the FERFs are unaffected. Because of the short-range nature of monopole FERFs, for nonbonded interactions (water- $F^-$ , water- $Na^+$ , water- $Mg^{2+}$ ), the addition of monopole FERFs does not change the polarization significantly ( $<1$  kcal/mol). The other orbital contraction stabilization energies estimated for the molecules above also closely match their monopole FERF calculation (see Table 1).

**Table 1. Comparison of Estimated Orbital Contraction Effects with Monopole FERF Polarization<sup>a</sup>**

	estimate	monopole FERF
H-H	21.3	20.9
Li-H	3.2	2.2
Li-Li	0.6	0.1
Be-H	11.3	11.3

<sup>a</sup>Energies in kcal/mol.

Monopole FERFs also allow us to quantify the importance of orbital contraction effects in the bonds to atoms with more than s orbitals (in which the distinction between contraction and polarization may be less clear). There are now three main polarization effects present in the ALMO-EDA POL term: rehybridization, contraction, and electric polarization. We therefore describe a polarization decomposition framework for bonded interactions.

The first term, rehybridization, may be defined as the energy stabilization due to rotations of the beta hole in the span of the alpha space. This is captured in ALMO-EDA as variational optimization between the doubly occupied and singly occupied orbitals (these orbitals were optimal for the fragments, not the

supersystem). Consider an F atom: The 2s orbital is doubly occupied, as are two of the 2p orbitals; one 2p orbital (which will define the bond axis) is singly occupied. Once there is another atom on the bond axis,  $2s(\uparrow\downarrow)-2p(\uparrow)$  orbital mixing results in the two sp-orbital hybrids, one of which is double occupied and pointing away from the bond and one of which is singly occupied and pointing toward the bond.

The contraction effect is determined by variationally optimizing the rehybridized fragments with the monopole FERFs. Although a collection of monopole FERFs on different centers in a nondiatom molecule could, in theory, alter the multipole moment of the fragment, in practice, we found this to not be a large effect, and the dominant effect of inclusion of monopole FERFs was, in fact, to allow for orbital contraction.

Finally, optimization of the orbitals with MDQ FERFs determines the electric polarization. The balance of the FERF POL term (after removing rehybridization and contraction) is ascribed to electric polarization. This term corresponds to the energy change due to the fragments polarizing in the electric field of the other fragments and is discussed at length in ref 37. Calculated polarization decomposition values are given in Tables 2 and 3 along with the CT term and the total CAS(2,2) interaction energy (i.e., the bond energy). These data were obtained from the bonded ALMO-EDA<sup>38</sup> (summarized in the Supporting Information) with a CAS(2,2) wave function and therefore do not include dynamic correlation, and so magnitudes of the contributions would likely be slightly larger (by 1–5 kcal/mol) than the values presented here if dynamic correlation was included.

It is interesting to separate orbital contraction from polarization as the former can be identified as the orbital response without change of multipole moment, while the latter is the orbital response with change of multipole moment. In this sense, they are fundamentally different as orbital contraction is an entirely quantum mechanical effect, while polarization can, at least to some extent, be understood classically. As a result, contraction and polarization do not follow the same trends (See Tables 2 and 3). It becomes immediately clear that when hydrogen is not involved in the bond of interest, orbital contraction becomes a very minor part of the bond stabilization. This may be understood because the



Table 2. Orbital Contraction Stabilization for E–H and E–CH<sub>3</sub> Bonds (basis = aug-cc-pCVTZ)<sup>a</sup>

	–H					–CH <sub>3</sub>				
	rehyb	CON	POL	CT	tot	rehyb	CON	POL	CT	tot
H	0.0	–20.9	–3.9	–4.5	–95.3	–3.0	–15.6	–7.7	–16.3	–103.8
HBe	0.0	–11.0	–2.9	–5.7	–83.2	–8.5	–1.9	–6.4	–38.2	–87.1
H <sub>2</sub> B	–0.6	–14.2	–5.3	–7.7	–97.7	–8.5	–0.8	–8.2	–35.2	–101.1
H <sub>3</sub> C	–3.0	–15.6	–7.7	–16.3	–103.8	–9.4	–1.0	–7.9	–35.9	–96.8
H <sub>3</sub> CCH <sub>2</sub>	–3.4	–15.3	–7.6	–16.0	–101.1					
H <sub>2</sub> N	–60.9	–22.7	–11.6	–42.8	–97.5	–107.4	–0.5	–15.3	–66.9	–81.4
HO	–33.1	–27.4	–5.6	–73.1	–103.4	–58.7	–1.5	–15.7	–94.7	–84.5
F	–23.1	–34.6	–14.4	–98.6	–114.6	–38.1	–1.4	–37.7	–113.6	–97.0
H <sub>3</sub> Si	–0.3	–10.8	–6.0	–5.5	–85.3					
F <sub>3</sub> Si	–0.1	–13.0	–5.7	–4.4	–93.7					

<sup>a</sup>Energies in kcal/mol.Table 3. Orbital Contraction Stabilization for E–F Bonds (basis = aug-cc-pCVTZ)<sup>a</sup>

	rehyb	CON	POL	CT	tot
H	–23.1	–34.6	–14.4	–98.6	–114.6
H <sub>3</sub> C	–38.1	–1.4	–37.7	–113.6	–97.0
F	–8.7	–0.9	–17.3	–59.0	–14.7
H <sub>3</sub> Si	–35.0	–0.6	–56.2	–168.0	–129.7
F <sub>3</sub> Si	–45.0	–1.9	–65.6	–138.9	–141.4
Li	–0.2	–0.1	–13.4	–128.6	–103.4

<sup>a</sup>Energies in kcal/mol.

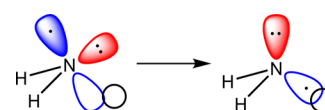
absence of a core in H means that contraction allows direct access to the nucleus without much additional electron–electron repulsion. For atoms with both a core and valence, to prevent significant increases in intershell electron–electron repulsion, *all* of the shells of the atom have to contract, which would result in too great of an increase in kinetic energy as well as increase the intrashell electron–electron repulsion from compressing the doubly occupied core into a smaller volume. This leads to relatively little energetic stabilization on orbital contraction for these atoms. Small changes in the orbital extent are also more consequential when the orbital is already small because the electron is deeper in the nuclear potential. The effect of orbital contraction in hydrogen-containing bonds is to restore virial balance after the kinetic energy stabilization of bond formation. In non-H atom bonds, we find that this virial balance restoration is *not* accomplished by orbital contraction but by other effects, such as polarization and charge transfer. The relatively high CT contributions for non-H atom bonds may be due to the extremely high ionization energy of hydrogen relative to larger atoms and molecules, which disfavors ionic-type stabilization.

Another way to think about the increased importance of orbital contraction with H atoms is to note that all bonds are relatively similar in energy (20–150 kcal/mol) on the scale of total electronic energy and therefore the kinetic energy stabilization on bond formation as a proportion of the total electronic energy of the system shrinks extremely rapidly as system size increases beyond hydrogen. Hence the degree of virial upset is significantly less, which allows virial balance to be restored by polarization and CT alone (which have much more modest effects on kinetic and potential energies). Specifically, the kinetic energy stabilization after spin-coupling in H<sub>2</sub> is 156.0 millihartree (compared with 167.8 as calculated by the method of Ruedenberg<sup>43</sup>), while the potential energy destabilization is 50.9 millihartree (compared with 58.7 as

calculated by Ruedenberg). This leads to a virial ratio of 2.31. After orbital contraction, the kinetic energy increases by 291.1 millihartree and the potential energy decreases by 324.3 millihartree, leading to a virial ratio of 2.003. After CT, the total orbital deformation has increased kinetic energy by 319.4 millihartree and decreased potential energy by 366.0 millihartree (compared with Ruedenberg's 320.1 and 363.3, respectively), leading to a final virial ratio of 1.99. Because all (single) bonds have broadly similar changes to kinetic and potential energy (owing to their similar bond strengths), the virial ratio is less affected after the initial kinetic energy stabilization for systems with large total electronic energy (i.e., core electrons).

To be clear, the present analysis does not disagree with the considerable work studying the bonds in H-atom-containing bonds. Indeed, this more complex orbital contraction situation was alluded to recently by Ruedenberg.<sup>17</sup> Explicit calculation for larger molecules unfortunately combined polarization and contraction into a single term, obscuring the fact that orbital contraction is not significant in non-H atom bonds.<sup>18</sup>

The rehybridization energies contained in Tables 2 and 3 show very interesting trends as well. Such energies are zero by definition on atoms such as H that do not naturally form hybrid orbitals and are also very small on fragments such as pyramidal CH<sub>3</sub>, where the odd electron is correctly “pre-hybridized”. By contrast, on F, OH, and NH<sub>2</sub>, the rehybridization energy can be quite large because substantial changes occur in the orbital containing the odd electron. For instance, an electron initially in the p<sub>z</sub> orbital of F is rearranged to occupy an orbital whose shape resembles that of an sp orbital. Even larger changes occur in the NH<sub>2</sub> fragment, yielding a substantial improvement in spin-coupling. These changes are illustrated in Figure 2. Finally, it can be observed by comparing rehybridization energies from Tables 2 and 3 that single bonds to fluorine yield rehybridization energies that are larger than the sum of the individual values seen in bonds to H. This is consistent with obtaining even better spin-coupling due to rehybridization in cases where both fragments can meaningfully do so.



**Figure 2.** Rehybridization of the amine radical from the free to “prepared” state with only large orbital lobes shown. The singly occupied orbital is shown in blue, the doubly occupied orbital is in red, and the hydrogen s orbital is in black.

In summary, fragment polarization during bond formation can be broken into three main effects: rehybridization, contraction, and electric polarization. Rehybridization is defined through mixing of doubly and single occupied fragment orbitals and provides substantial energy stabilization for functional groups like  $\text{NH}_2$ ,  $\text{OH}$ , and  $\text{F}$ , as discussed above. Orbital contraction effects (which were previously largely absent from the ALMO FERF polarization scheme) can be captured by inclusion of a “monopole” FERF term calculated as the response to the addition of a point charge at the nucleus. This polarization decomposition reveals that orbital contraction, although an important effect in bonds to hydrogen, is fairly minor for heavier-atom bonds. Virial balance is restored in such systems by electric polarization and charge transfer.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b00766.

Brief description of the ALMO EDA method for bonds, computational notes, verification of using all atoms for constructing monopole FERFs, and geometries for bonds. (PDF)

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### Notes

The authors declare no competing financial interest.

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