Anisotropic Charge Distribution and Anisotropic van der Waals Radius Leading to Intriguing Anisotropic Noncovalent Interactions

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Although group (IV–VII) nonmetallic elements do not favor interacting with anionic species, there are counterexamples including the halogen bond. Such binding is known to be related to the charge deficiency because of the adjacent atom’s electron withdrawing effect, which creates $\sigma$/p-holes at the bond-ends. However, a completely opposite behavior is exhibited by N$_{2}$ and O$_{2}$, which have electrostatically positive/negative character around cylindrical-bond-surface/bond-ends. Inspired by this, here we elucidate the unusual features and origin of the anisotropic noncovalent interactions in the ground and excited states of the 2nd and 3rd row elements belonging to groups IV–VII. The anisotropy in charge distributions and van der Waals radii of atoms in such molecular systems are scrutinized. This provides an understanding of their unusual molecular configuration, binding and recognition modes involved in new types of molecular assembling and engineering. This work would lead to the design of intriguing molecular systems exploiting anisotropic noncovalent interactions.

Molecular recognition and self-assembly of biomolecules and nanomaterials are governed mostly by non-covalent interactions including hydrogen bonding, $\pi$-interactions, and halogen bonding. Quite often, molecular conformations are determined by electrostatic interactions which are generally described by isotropic atomic charges. However, atomic charges in molecules are not isotropic. As a simple example, the $\sigma_{g}$ molecular orbital (MO) of an H$_{2}$ molecule shows overlap between 1s atomic orbitals (AOs) of the two atoms. This overlap increases the electron density ($\rho_{c}$) between the two nuclei (i.e., over the cylindrical surface surrounding the bond), which results in negative electrostatic potential (ESP). Then, the decreased $\rho_{c}$ outside the two nuclei (around bond-ends) results in positive ESP. Thus, the quadrupole moment ($Q_{zz}$) for the case where the two atoms are along the z-axis is positive (0.45 debye$\cdot$Å). Such phenomena could be expected for all the homonuclear diatomic molecules regardless of the $\sigma$- or $\pi$-type overlap, as can be seen from ESP maps of H$_{2}$ ($\sigma_{g}$ MO) and C$_{2}$ ($\pi_{u}$ MO) shown in Figure 1a. The anisotropic charge distributions result in highly direction-specific interactions best exemplified by halogen bonding, the origin of which is generally explained by the concept of $\sigma$-hole. This anisotropy in charge distribution is visualized in F$_{2}$ and Cl$_{2}$ ESP maps (Figure 1a). It can be understood as a “hole” residing in the antibonding $\sigma^{*}$-orbital. Since this $\sigma$-hole, in principle, forms at both ends of every $\sigma$-bond, one might expect that this concept would be applicable to all the elements.

In this regard, we have calculated the ESP maps for homonuclear diatomic molecules of second and third row elements. We note that, for N$_{2}$ and O$_{2}$, the covering of $\sigma$-hole by the nonbonding electrons inverts the typical anisotropy (Figure 1a). N$_{2}$ shows negative ESP at bond-ends and positive ESP around the cylindrical-bond-surface. A similar result was also reported very recently by Hobza and coworkers. A simple AO-overlap concept cannot explain the N$_{2}$ case. The positive ESP around the cylindrical-bond-surface between two N nuclei of the N=N bond is even more difficult to understand, since compounds with C=C bonds usually undergo facile reactions with electrophiles.

To understand this puzzling anomaly, we investigated the difference in MOs and natural bonding orbitals (NBOs) for the ground states of N$_{2}$, O$_{2}$, F$_{2}$, P$_{2}$, S$_{2}$, and Cl$_{2}$ and their first excited states ($'\text{N}_{2}$, O$_{2}$, F$_{2}$, P$_{2}$, S$_{2}$, and Cl$_{2}$).
tCl2), where the superscript “t” denotes triplet-state. The differences in orbital hybridization, bond-length, and nuclear-charge turn out to be important factors in anisotropy. To investigate the anisotropy effect on the measurable quantities, we studied the interaction of homonuclear diatomic molecules with themselves, positively/negatively charged ions (Na+, Cl2), a water molecule and a benzene molecule, using Møller-Plesset second-order perturbation theory (MP2) and coupled-cluster theory of singles, doubles and perturbative triples excitations (CCSD(T)) at the complete basis set (CBS) limit. Here we discuss the anomaly arising from the charge anisotropy of N2 and 'O2 in particular.

**Results**

Ground states of N2, 'O2 and F2. ESP contour maps of representative homonuclear diatomic molecules at their optimized geometries are shown in Figure 1a along with their bond distance (d) and Qzz. Inspection of the Qzz values of second-row homonuclear diatomic molecules ('B2, C2, N2, 'O2, F2) reveals that Qzz decreases abruptly to a negative value at N2, and again increases to a positive value at F2. This sign change in Qzz indicates the inversion of anisotropy at N2. Consistent to this observation, the ESPs of N2 and 'O2 are negative at bond-ends and positive around the cylindrical-bond-surface, unlike other ground state species. The
issue of $Q_{ne}$ and its relation to ESP was also addressed in literature recently\textsuperscript{28,30}.

To find a qualitative reasoning for the prominent difference between N\textsubscript{2} and F\textsubscript{2}, we take both $\rho_s$ and nuclear charge into account. Nitrogen has a smaller effective nuclear-charge ($Z_{\text{eff}}(\text{N}_2) = 3.83$) than fluorine ($Z_{\text{eff}}(\text{F}_2) = 5.10$)\textsuperscript{14}. Therefore, at some distances from the bond-ends the $\rho_s(N)$ becomes higher than $\rho_s(F)$, as can be seen from the $\sigma$-bonding MOs shown in Figure 1b. Furthermore, since the bond length of N\textsubscript{2} (1.10 Å) is much shorter than that of F\textsubscript{2} (1.42 Å), the large electron-population required by the N=N bond cannot be accommodated within such a small space between the two N nuclei. A nodal plane bounded by a positively charged region near each nucleus and a negatively charged region somewhat away from the N nucleus is formed outside each N nucleus. This is because a large fraction of electron-population in a large space outside the N nucleus (though not dense) screens out the small effective positive charge of the N nucleus beyond a certain distance from the nucleus. As a result, a small portion of the total electron-population in the N=N bond and the summed nuclear-charge of two closely adjacent N nuclei make the cylindrical-bond-surface electrostatically positive. In contrast, a small electron-population of the F-F single bond can be easily accommodated in a reasonably large space between the two F nuclei. In F\textsubscript{2}, a large fraction of the total electron-population stays around the bond-ends, whereas only a small portion of the total electron-population stays outside the two F nuclei. Therefore, the regions outside the F-F bond-ends are positively charged due to the large nuclear-charge and small electron-population, whereas the cylindrical-bond-surface between the two F nuclei is negatively charged due to the large fraction of electron-population. In the case of the ground triplet state $\text{O}_2^*$, its molecular size and electronic properties are between those of N\textsubscript{2} and F\textsubscript{2}, as visualized from their $\sigma$-bonding MOs (Figure 1b). The bond-ends are nearly neutrally charged or very weakly positively charged. Even though the effective charge of O ($Z_{\text{eff}}(\text{O}_2) = 4.45$) is almost in between those of N and F, the $\text{O}_2^*$ double-bond-length (1.21 Å) is still short, closer to the bond-length of N\textsubscript{2} than F\textsubscript{2}, and so the cylindrical-bond-surface of $\text{O}_2^*$ is still positively charged, and its bond-ends are nearly neutral but weakly electrostatically negative. The most electrostatically positive site is the flat potential region $-60 < \theta < 60$ around the O nucleus.

To explain in a more quantitative manner, we computed the NBOs of N\textsubscript{2}, $\text{O}_2$, F\textsubscript{2} and their third-period analogues. From the s-p hybridization characters of $\sigma$-bond pairs lying on the bond axis, we find an important difference in $\rho$-character among the lone pairs on N\textsubscript{2} (37%), O\textsubscript{2} (18%) and F\textsubscript{2} (5%) (Supplementary Table S1), which is due to the bond-length, the energy-gap between s and p orbitals, and nuclear-charge. For this reason, the 2s-electrons of O atoms spill out of the bonding region upon the formation of N\textsubscript{2}, making bond-ends negatively charged. On the other hand, the 2s-electrons of F atoms stay localized upon the formation of F\textsubscript{2} (not compensating for the $\sigma$-holes at bond-ends), making bond-ends positively charged. The charge anisotropy of $\text{O}_2^*$ lies in between those of N\textsubscript{2} and F\textsubscript{2}, featuring a near-flat ESP on the density isosurface. As for a large nuclear-charge, the s-orbital is favored in order to screen the nuclear-charge but not sufficient enough, giving positive ESP around the bond-ends. For a small nuclear-charge, the somewhat p-like electron-population can be widely dispersed, resulting in negative ESP due to the still significant $\rho_s$ in the bond-ends. This can be seen from the ESP map of CO (isos electronic to N\textsubscript{2}), where the electron-population around the C atom is dispersed, while that around the O atom is highly contracted, as noted from the HOMO of CO in Figure 1b.

**Ground states of P\textsubscript{2}*, S\textsubscript{2} and Cl\textsubscript{2}**. The anisotropy of ESP of the third-period equivalents is less prominent than their second-period equivalents. Owing to the increased bond-length, the ESP is negative near the mid-region of the cylindrical-bond-surface because the effect of two nuclear-charges is sub-additive. The lengthening of bonds also leads to the decrease in 3s-3p orbital mixing, resulting in the localization of $\sigma$-lone pairs in 3s-orbitals. For example, the bond length of Cl\textsubscript{2} (1.99 Å) is longer than that of F\textsubscript{2}. Its bond-ends are more positively charged than that of F\textsubscript{2}, but the overall pattern of ESP is alike. Analogously, one could expect that the ESP of the triplet ground state $\text{S}_2$ is also similar to that of $\text{O}_2$. However, since the S = S bond-length (1.90 Å) is much longer than that of $\text{O}_2$ (1.21 Å), the ESP contribution from the two nuclei is rather weak at the mid region of the cylindrical-bond-surface of $\text{S}_2$. Therefore, the mid-region of $\text{S}_2$ is electrostatically negative unlike that of $\text{O}_2$, which in turn results in electron deficiency in the S2 bond-ends. Overall, $\text{S}_2$ behaves rather similarly to F\textsubscript{2}/Cl\textsubscript{2}. P\textsubscript{2} forms a triple bond with one $\sigma$-bonding and two $\pi$-bonding MOs. However, the large internuclear separation (1.92 Å) makes the mid-bond highly electrostatically negative, thereby resulting in electrostatically positive bond-ends. Thus, P\textsubscript{2} behaves oppositely to N\textsubscript{2}, but rather similarly to F\textsubscript{2}/Cl\textsubscript{2} despite the fact that N and P belong to the same group V.

**Excited States**. The anisotropic ESPs of the excited states of homonuclear diatomic molecules are also shown in Figure 1a. ESP patterns of the excited states are in many cases opposite to the ground state. Such trends appear for the excited state of all other homonuclear diatomic molecules. Since the excited states show ESP patterns different from or opposite to the corresponding ground state, one can imagine laser-controlled on-off motion which can lead to the design of molecular flippers or nanomechanical devices including molecular switches\textsuperscript{29,30}.

We consider the cases where N\textsubscript{2}, $\text{O}_2$, and F\textsubscript{2} are excited to triplet, singlet and triplet states, respectively. The excited triplet $\text{N}_2$ has one $\sigma_g$-bonding, one $\pi_{ux}$-bonding, one half-occupied $\pi_{u}$ bonding, and one half-occupied $\pi_{uy}$-antibonding. Since one of the $\pi$ bonds is lost upon excitation, the bond distance is lengthened to 1.22 Å. As such, the electron-population between two N nuclei in ‘N\textsubscript{2}’ no longer spills over outside the N nuclei, in contrast to the overcrowded electron-population between the two closely bound N nuclei in the ground singlet N\textsubscript{2}. The large electron-population between two N nuclei in the $\pi_{uy}$ MO cancels the depleted electron-population in the $\pi_{uy}$ MO. Additionally, the $\sigma_g$-bonding makes the bond-ends electrostatically positive along the z-axis by the overlap between the two $p_z$-orbitals. On the other hand, the $\pi_{ux}$ MO induces negative ESP due to highly increased $\rho_s$ on the top and bottom of the cylindrical-bond-surface (top view of ‘N\textsubscript{2}’ in Figure 1a), while it introduces positive ESP due to the depleted $\rho_s$ on the front and back of the cylindrical surface (bottom front view of ‘N\textsubscript{2}’ in Figure 1a). The effective MOs for N\textsubscript{2} are a half $\sigma_g$ bond, one $\pi_{ux}$ bond and a half $\pi_{uy}$ bond. In the case of the singlet $\text{O}_2$, one $\sigma_g$ bond, two $\pi_u$ bonds, and one $\pi_{uy}$ bond (the effective MOs: one $\sigma_g$ bond, one $\pi_{ux}$ bond) behave similarly as in the N\textsubscript{2} case. Also, in the case of the singlet F\textsubscript{2}, one $\sigma_g$ bond, two $\pi_u$ bonds, one and a half $\pi_{ux}$ bond and a half $\pi_{uy}$ bond behave similarly as in the N\textsubscript{2} case. This is explained by cancellation between bonding and antibonding such that the resulting effective MOs are a half $\sigma_g$ bond and a half $\pi_u$ bond, which is similar to the singlet $\text{O}_2$ and the triplet ‘N\textsubscript{2}’. The excited states $\text{P}_2$, $\text{S}_2$ and Cl\textsubscript{2} show similar trends, as discussed for ‘N\textsubscript{2}’ and $\text{O}_2$. In the ‘$\text{P}_2$’ case, the contrast between the maximum and minimum ESP is slightly weaker than $\text{S}_2$ and Cl\textsubscript{2}.

Even when an electron is fully excited to a cationic state, the anisotropic charge distribution can still be seen though the polarization effect is diminished by the charge effect. The discussion along with the ESPs of ionized homonuclear diatomic molecules and the issues of MO energy level diagrams\textsuperscript{31,32} for the charged states is in Supplementary note 1.

**van der Waals atomic radii in homodiatomic molecules**. In molecular interactions the electrostatic interactions ($E_{el}$) often govern molecular structures. The van der Waals interactions composed of the dispersion energies ($E_{disp}$) and exchange repulsion energies ($E_{exch}$) determine molecular size. The van der Waals radii of atoms...
Interactions of homonuclear diatomic molecules with ionic species Na⁺ and Cl⁻. Physical manifestation of the ESP maps can be understood by considering the interaction energy between homonuclear diatomic molecules with a positively or negatively charged ion (Na⁺ or Cl⁻) (Figure 3). The bond-ends of N₂ favor cationic species, whereas those of F₂/Cl₂/S₂ favor anionic species. O₂ favors cationic species at bond-ends, but behaves somewhat isotropically towards anionic species. P₂ behaves nearly isotropically towards cationic species, but strongly favors the θ = ±60° direction towards anionic species.

N₂ strongly interacts with Na⁺ around the bond-ends (interaction energy Eₓ = −30 kJ/mol at the distance from the ion to the nearest nucleus (dₘₚ) of 2.53 Å according to the CCSD(T)/CBS energy and CCSD(T)/aVTZ optimized geometry. In contrast, F₂ strongly interacts with Na⁺ around the cylindrical mid-surfaces of the bond (Eₓ = −14 kJ/mol at the distance from the ion to midpoint of the two nuclei (dₘₚ) of 2.54 Å. O₂ behaves between N₂ and F₂, but slightly more closely to N₂, because Na⁺ favors the bond-ends of O₂ (Eₓ = −16 kJ/mol, dₘₚ = 2.57 Å). P₂ shows almost isotropic potential (Eₓ = −37 kJ/mol at dₘₚ = 3.05 Å; Eₓ = −34 kJ/mol at dₘₚ = 2.98 Å). S₂ strongly favors Na⁺ around the cylindrical mid-surfaces of the bond (Eₓ = −34 kJ/mol at dₘₚ = 2.91 Å; Eₓ = −18 kJ/mol at dₘₚ = 2.92 Å). Cl₂ shows Eₓ = −34 kJ/mol on the cylindrical mid surface (dₘₚ = 2.76 Å), but no binding along the z axis.

On the other hand, for Cl⁻, N₂ strongly interacts with it around the mid-point of the cylindrical-bond-surface (Eₓ = −9 kJ/mol at dₘₚ = 3.55 Å); in contrast, F₂ strongly interacts along the bond-ends along the z axis (Eₓ = −90 kJ/mol, dₘₚ = 1.95 Å). O₂ behaves almost in between N₂ and F₂, but again slightly more closely to N₂, because the cylindrical-bond-surface is more favored (Eₓ = −6 kJ/mol at dₘₚ = 3.57 Å; Eₓ = −7 kJ/mol at dₘₚ = 3.40 Å). P₂ shows the strongest interaction (Eₓ = −62 kJ/mol) at the distance from the midpoint of a molecule to an ion around θ = 60° from each nucleus (dₘₚ) (3.07 Å). S₂ gives Eₓ = −40 kJ/mol at the bond-ends (dₘₚ = 2.97 Å), and Cl₂ shows Eₓ = −102 kJ/mol at the bond-ends (dₘₚ = 2.33 Å). As such, we confirmed that the interaction of homonuclear diatomic species with closed-shell ions is mainly determined by the ESP of the diatomic species.

Interactions of the homodiatomic molecules with H₂O. Water moisture is present in air, which is composed predominantly of N₂ and O₂. In clouds, on wet surfaces, and on the surface of water in rivers, lakes, and sea, the water molecules and clusters interact with N₂ and O₂ in the atmosphere. Even though individual interaction is small in magnitude, their abundance in the huge atmospheric space on earth is enormous. For this reason, understanding their accurate interactions is highly important. Figure 4a shows the interactions of H₂O with N₂/O₂/O₃ and F₂/N₂ interacts strongly with the H of H₂O on the bond-ends (interaction energy Eₓ = −5.17 kJ/mol) and weakly with the O of H₂O on the cylindrical-bond-surface (Eₓ = −2.96 kJ/mol). However, in the case of F₂, the F-F bond-ends interact strongly with the O of H₂O (Eₓ = −5.71 kJ/mol), while the cylindrical-bond-surface interacts with the O of H₂O (Eₓ = −4.70 kJ/mol). In the cases of O₂ and O₃, the O at an edge of the

**Figure 2** | Anisotropic hard wall distance (Å) of an atom N/O/F in the molecule N₂/O₂/F₂ for three different orientations (0°, 90°, central): N (3.29, 3.26, 3.34), O (3.03, 3.11, 3.18), F (2.78, 3.02, 3.08) at the CCSD(T)/CBS level (see text for van der Waals radius).
cylindrical-bond-surface (making an angle of \( \sim 60^\circ \) with respect to the z axis) interacts with H of \( \text{H}_2\text{O} \) \((E_e = -2.33 \text{ kJ/mol} \) and \( E_a = -6.37 \text{ kJ/mol} \) respectively). At the interface between water and the atmosphere, the H atoms in \( \text{H}_2\text{O} \) tend to interact strongly with the bond-ends of \( \text{N}_2 \), while the interaction with \( \text{O}_2 \) is somewhat weaker. Given that the O atoms in water are better stabilized by coordinating H atoms of other water molecules than the H atoms stabilized by O atoms of other water molecules, as noted in water clusters 37 and water surfaces 38,39, such interaction would help H atoms in the water surface interact with the bond-ends of \( \text{N}_2 \) molecules.

**Interactions in homo-dimers and hetero-dimers of the homonuclear diatomic molecules.** The structures of homo-dimers and hetero-dimers for the homonuclear diatomic molecules are shown in Figure 4b. Binding energies of these structures are governed by the electrostatic interaction and van der Waals interaction. Using
Figure 4 | Interactions of homonuclear dimers X₂ (or Y₂) with water, X₂/Y₂, and benzene. (a) Interaction of a single water molecule with N₂/O₂/O₂/F₂. The binding energies Eᵢ are given for both the most stable structure interacting with H of a water molecule and that with O of a water molecule. For the less stable structure between the H and O interaction cases, the water molecule is given with a half-tone color. (b) Interactions of N₂ with N₂ and F₂. (c) Interactions for benzene-X₂ (X = N, O, O, F, Cl). All binding energies Eᵢ are given in kJ/mol at the CCSD(T)/CBS level. Each distance marked in a dotted line is given in Å (in parentheses) for the CCSD(T)/aVTZ optimized geometry (In the case of benzene-X₂, only the interacting distance was optimized at the CCSD(T)/aVTZ level using the BSSE-corrected MP2/aVTZ geometry).

Interactions of the homonuclear diatomic molecules with benzene. The interactions of homonuclear diatomic molecules with benzene (Bz) are shown in Figure 4c. Hobza and coworkers carried out a similar study. Bz has negatively charged electron clouds both above and below the Bz-plane, while being surrounded by positively charged H atoms around the edge. The parallel structure is the most stable (Eₑ = −1.24 kJ/mol) and the L-shape (Eₑ = −1.22 kJ/mol). In the Pd structure the negatively charged bond-end of one molecule is on top of the positively charged bond-surface of the other molecule, and vice versa. In the L-shape the negatively charged bond-end of one molecule is directly pointing to the positively charged bond-surface of the other molecule. In both Pd and L shapes, the electrostatic energy (Eₑ = −0.74 kJ/mol, respectively) is important. In the case of the hetero-molecular interaction between N₂ (which has electrostatically negative bond-ends) and F₂ (which has electrostatically positive bond-ends), a linear structure is the most stable in the potential energy surface (Eₑ = −2.24 kJ/mol) where the key energy contribution is the electrostatic energy (Eₑ = −2.58 kJ/mol). In the homo-dimer systems, while Eₑ is important, the dispersion term Е₅₂ related to the van der Waals radius and van der Waals interaction can also be important in determining their structures (see Supplementary Note 2 for the details).
is very large, the anisotropic charge distribution in $A_2$ plays a very important role in determining the structures.

### Heteronuclear diatomic molecules

The ESP maps for heteronuclear diatomic molecules of nonmetallic elements are computed at MP2/aVTZ level. The charge analysis according to ESP (somewhat different from the NBO charge analysis, for example, as in CO for which the NBO charges give the wrong dipole direction) of heteronuclear diatomic molecules shows: $C_2$N, $C_2$O, $C_2$F, $N_2$F, $O_2$F, $N_2$P, $O_2$P, $F_2$Cl, $C_2$P, $C_2$S, $C_2$Cl, $N_2$S, $N_2$Cl, and $O_2$Cl (Figure 5). This result is counterintuitive, since the more electronegative element is positively charged except for a few cases. Therefore, we speculate that the electrons tend to be populated to reduce the electrostatic imbalance, i.e., to neutralize the electrostatical positivess around the nuclei, but not sufficiently. Therefore, the regions around the nuclei with the larger nuclear-charge (i.e., higher electronegativity) tend to be electrostatically positive except for the group I–III elements which tend to be strongly electrostatically positive. Indeed, such a trend holds for almost all the cases of the above hetero-diatomic molecules. As for the three exceptional cases $C_2$N, $N_2$O, and $O_2$F (three left-top ESP maps in Figure 5), the two nuclear-charges are similar (the nuclear charge difference between two atoms is only 1).

### Discussion

We analyzed the anisotropic charge distribution and anisotropic van der Waals radii of atoms in diverse diatomic molecules to understand intriguing novel molecular interactions. We scrutinized molecular interactions of various diatomic molecules of Group (IV–VII) elements (which disfavor anionic species) with themselves, an cation (Na$^+$)/anion (Cl$^-$), H$_2$O, and benzene. Though there have been some discussions on such group elements interacting with anionic sites or themselves, the clear understanding was lacking. For accurate description of their subtle interactions, we note that the anisotropy in charge distribution around the atoms which arise from a number of factors including MO, nuclear charge and bond length should be considered. The fundamental understanding of the origin and characteristic features of anisotropic noncovalent interactions could be utilized in novel molecular recognition, assembling, engineering, and dynamical control.

### Methods

The ESP at each point in space is defined as in Equation (1), where $Z_i$ and $R_i$ are the nuclear charge and position, respectively.

$$V(r) = \sum Z_i \frac{\rho_i(r)}{|r-R_i|} dr$$  (1)

The quadrupole moment $Q_{zz}$ is defined as in Equation (2), which becomes more negative/positive as the electron-population gets contracted/expanded toward the

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Figure 5 | ESP of heteronuclear diatomic molecules (MP2/aVTZ). $q$: NBO charge (au), $\mu$: dipole moment (debye), where the subscript A designates the atom to which the dipole direction is pointing from the molecular center. The dipole vectors are along the right direction except the left direction of the three cases of CN, NO, and OF (for which the nuclear charge difference between two atoms is only 1).
z-axis (i.e., as the electron-population is more oblated/prolated in the diatomic molecule).

\[
Q_{\alpha\beta} = \left(3\zeta^2 - 1\right) \sum_i Z_i \mu(r - R_i) - \rho_{\alpha\beta}(r) \, dr
\]

The CCSD(T)/CBS limit (\(E_{CBS}\)) of an interaction energy (\(E\)) is evaluated based on the extrapolation method\(^{46}\) exploiting that the basis set error in the electron correlation energy is proportional to \(N^{-4}\) for the aug-cc-pVNZ (avNZ) basis set (\(E_{CBS} = [E_{CBS}^{N = 9} - E_{CBS}^{N = 7}] / (N(N - 1))\)). Here, CCSD(T)/aVZ and CCSD(T)/aVQZ energies at the CCSD(T)/aVTZ optimized geometries were used for the extrapolation to the CBS limit. Ab initio calculations were carried out using Gaussian [Frish, M. J. et al. Gaussian 09, revision A.02 (Gaussian, Inc., 2009)] and Molpro [Werner, H.-J. et al. Molpro quantum chemistry package, version 2012.1, http://www.molpro.net/ (2012) (date of access: 01/06/2012)] packages.

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