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ABSTRACT

This paper accounts for a general procedure of bonding analysis that is, expectedly, adequate to describe any type of interaction involving the noble-gas (Ng) atoms. Building on our recently proposed classification of the Ng–X bonds (X = binding partner) [New J. Chem. 44, 15536 (2020)], these contacts are first distinguished into three types, namely, A, B, or C, based on the topology of the electron energy density $H(\mathbf{r})$ and on the shape of its plotted form. Bonds of type B or C are, then, further assigned as B-loose (B^l) or B-tight (B^t) and C-loose (C^l) or C-tight (C^t) depending on the sign that $H(\mathbf{r})$ takes along the Ng–X bond path located from the topological analysis of $\rho(\mathbf{r})$, particularly at around the bond critical point (BCP). Any bond of type A, B^l/B^t , or C^l/C^t is, finally, assayed in terms of contribution of covalency. This is accomplished by studying the maximum, minimum, and average value of $H(\mathbf{r})$ over the volume enclosed by the low-density reduced density gradient (RDG) isosurface associated with the bond (typically, the RDG isosurface including the BCP) and the average $\rho(\mathbf{r})$ over the same volume. The bond assignment is also corroborated by calculating the values of quantitative indices specifically defined for the various types of interactions (A, B, or C). The generality of our taken approach should encourage its wide application to the study of Ng compounds.

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I. INTRODUCTION

The general inertness of the noble gases could suggest a limited variety of compounds and bonding motifs. Nothing further from the truth, the “inert” elements, in fact, are capable of forming quite different chemical bonds, ranging from weakest van der Waals contacts to strong covalent bonds. A variety that is, probably, unique in the periodic system. Krypton and, especially, xenon form numerous covalent compounds that are isolable under ordinary (or nearly ordinary) conditions.^{1–5} Helium, neon, and argon are inactive in mild environments but fixable into truly combined species when activated in ultra-cold matrices,^{6,7} in high-pressure devices,^{8,9} or in the ion sources of mass spectrometers.^{10,11} Furthermore, all the noble-gas (Ng) atoms, despite resistant to form true covalent or ionic bonds, are quite sensitive to the polarization by the binding partners and form non-covalent species ranging from

pure (or nearly pure) “dispersive” complexes to systems featuring appreciable contributions of induction and charge transfer (CT).¹² Over the years, the nature of the Ng–X interactions (X = binding partner) has been extensively investigated by various techniques of bonding analysis,¹³ including methods that rely on quantum chemical topology.^{14–16} The study of the electron density $\rho(\mathbf{r})$ of the landmark theory of Atoms in Molecules (AIM),¹⁷ of the electron localization function (ELF),^{18–20} and of the reduced density gradient (RDG) $s(\mathbf{r})$ and its related Non-Covalent Interaction (NCI) index^{21,22} is, in particular, quite informative about the bonding situation of Ng compounds.^{23–35} Working in the same context, we showed³⁶ that the bonding motifs of Ng compounds are also effectively described by studying the topology of the local electron energy density $H(\mathbf{r})$.^{17,37–39} Building on this first report, we examined a variety of Ng compounds,^{40–43} and we could recently propose a classification of the Ng–X bonds⁴⁴ that relies on the topology of $H(\mathbf{r})$,

on its graphed form, and on the values that this function takes over the volume enclosed by the RDG isosurfaces associated with the bond critical point (BCP) located on the Ng–X bond path (BP).¹⁷ The Ng–X bonds are, thus, distinguished into covalent (Cov), non-covalent (nCov), and partially covalent (pCov), and the latter are further assayed in terms of contribution of covalency. The nature and strength of the various interactions are also evaluated by quantitative indices defined in connection with the proposed classification. The employed method is independent of geometric criteria, robust with respect to the computational level, and suitable to make comparisons between different classes of Ng compounds. In the present study, we refined the adopted criteria of classification so to best distinguish, in particular, the character of interactions featuring major similarities in the topology of $H(\mathbf{r})$. As a matter of fact, formulated as presented here, our method of bonding analysis is, expectedly, adequate to describe any type of Ng–X interaction. To hopefully encourage its wide application, we are also reporting a detailed step-by-step procedure, aimed at also best clarifying the practical use of our taken approach.

This paper is organized as follows. After a brief account of the relevant computational details, we recall the major features of atomic and molecular $H(\mathbf{r})$, with emphasis on the situations occurring in Ng compounds. In this context, we illustrate the criteria adopted to classify the Ng–X bonds. We then formulate the step-by-step procedure of bonding analysis and, finally, discuss some exemplary systems taken from the recent literature.

II. COMPUTATIONAL DETAILS

The calculations were performed at the Møller–Plesset perturbation level of theory truncated at the second order (MP2)⁴⁵ using the Dunning's correlation consistent aug-cc-pVTZ basis set⁴⁶ (henceforth denoted as aVTZ). The Xe atom was treated with the aVTZ-PP basis set developed in conjunction with the Stuttgart/Cologne small-core (28 electrons) scalar-relativistic effective core potential (ECP-28).⁴⁷ As shown in our recent study,⁴⁴ the bonding analysis of Ng compounds performed at the MP2/aVTZ level produces results strictly similar to those obtained at the benchmark CCSD(T)/aVTZ. We also ascertained in our previous study⁴⁴ the generally good performance of the B3LYP/aVTZ, even though this computational level tends to underestimate the role of covalency and sometimes furnishes bond indices quantitatively different from the benchmark data. This suggests some caution in the use of DFT methods to describe the Ng–X bonds, especially from the quantitative point of view.

The calculations were performed with the Multiwfn program (version 3.8.dev)⁴⁸ using the wfx files generated from the Gaussian 09 package.⁴⁹ The geometries of the investigated species were taken from the literature^{44,50–53} or presently optimized at the MP2/aVTZ level of theory using Gaussian 09. The full Cartesian coordinates are given in Data S1 of the [supplementary material](#) (SM). The linear and planar (2D) plots of $H(\mathbf{r})$ were produced with the Multiwfn, the 2D plots including the standard contour lines belonging to the patterns $\pm k \times 10^n$ ($k = 0, 1, 2, 4, 8$; $n = -5$ to 6) and the contour lines to which belong the critical points located from the topological analysis of $H(\mathbf{r})$.

III. RESULTS AND DISCUSSION

A. The atomic $H(\mathbf{r})$

$H(\mathbf{r})$ ^{17,37–39} is the sum of the kinetic energy density $G(\mathbf{r})$ and the potential energy density $V(\mathbf{r})$,

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}). \quad (1)$$

The presently employed definition^{17,39} of $G(\mathbf{r})$ is given by the following equation:

$$G(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{\text{NO}} \eta_i |\nabla \varphi_i(\mathbf{r})|^2, \quad (2)$$

where the sum runs over all the occupied natural orbitals (NO) φ_i of occupation numbers η_i . The potential energy density $V(\mathbf{r})$ is evaluated¹⁷ from the local form of the virial theorem,

$$V(\mathbf{r}) = \frac{1}{4} \nabla^2 \rho(\mathbf{r}) - 2G(\mathbf{r}). \quad (3)$$

$G(\mathbf{r})$ is, invariably, positive, and $V(\mathbf{r})$ is, invariably, negative. Thus, $H(\mathbf{r})$ may be positive, negative, or null. In particular, in the inner atomic regions, $G(\mathbf{r})$ is, typically, lower than $|V(\mathbf{r})|$ and $H(\mathbf{r})$ is negative. On the other hand, in the outer atomic regions, $G(\mathbf{r})$ is, typically, higher than $|V(\mathbf{r})|$ and $H(\mathbf{r})$ is positive. Thus, in the simplest situations, $H(\mathbf{r})$ partitions the atomic space into just two regions, an inner one of negative values, indicated here as $H^-(\mathbf{r})$, and an outer one of positive values, indicated here as $H^+(\mathbf{r})$. Exemplary in this regard are the H atom and the Ng atoms He, Ne, Kr, and Xe. The corresponding 2D plots of the $H(\mathbf{r})$ are shown in Fig. S1 of the [supplementary material](#). For these systems, in the $H^-(\mathbf{r})$ region, the function is minimum (most negative) at the nucleus and progressively increases (sometimes passing for local maxima and minima) until becoming null at a distance, indicated as R^- , that is typical of each atom. For $R > R^-$, $H(\mathbf{r})$ is positive and becomes vanishingly small at the largest distances, passing through a point of maximum. The Ar atom differs from its congeners in that it features an additional inner $H^+(\mathbf{r})$ region, within which the function passes through a local point of maximum. An additional (more or less tiny) inner $H^+(\mathbf{r})$ sub-region is, indeed, common to all the second- and third-row atoms Be–F and Mg–Cl. In any case, as shown in Figs. S2 and S3, this does not preclude to clearly recognize the atomic space as partitioned in two major $H^-(\mathbf{r})$ and $H^+(\mathbf{r})$ regions. The only exceptions are the metal atoms Li and Na, possessing a peculiar outer $H^-(\mathbf{r})$ region between ~ 1 and ~ 3 Å. It should also be noted from Figs. S2 and S3 that the 2D graphs of B, C, O, F, Al, Si, S, and Cl look different for different plotting planes. For these open-shell species, in fact, the distances along x , y , and z at which the minima and maxima of $H(\mathbf{r})$ fall are not always identical, and the height of these critical points may also depend on the direction. Thus, when plotted in different planes, the contour lines of $H(\mathbf{r})$ can have different shapes. For example (see Fig. S2), the contour lines of C (assumed here to be $1s^2 2s^2 2p_x 2p_y$) are spherical in the xy plane but non-spherical in the two equivalent xz or yz planes. One also notes that, for atoms belonging to the same group, the size of the $H^-(\mathbf{r})$ region increases when going from the lightest to the heaviest congener(s). The $H^-(\mathbf{r})$ region, in fact, encloses the majority of the electronic

charge, and its size mirrors, in essence, the atomic radius. For example, particularly for the five Ng atoms, the populations of the $H^-(\mathbf{r})$ regions are 1.39 e (He), 8.96 e (Ne), 16.88 e (Ar), 34.84 e (Kr), and 52.73 e (Xe), and the corresponding values of R^- , 0.589 Å (He), 0.809 Å (Ne), 1.264 Å (Ar), 1.399 Å (Kr), and 1.595 Å (Xe), positively correlate with the values of the covalent radii (0.46, 0.67, 0.96, 1.17, and 1.31 Å, respectively⁵⁴).

B. The $H(\mathbf{r})$ of noble-gas compounds: Bonds of type A, B, or C

When the atoms form chemical bonds, their $H^+(\mathbf{r})$ and $H^-(\mathbf{r})$ regions combine in modes that signal the nature of the interaction. Particularly for Ng compounds, we showed in the previous studies^{36,44} that the various Ng–X contacts can be classified based on the topology of the molecular $H(\mathbf{r})$ and on the shape of its plotted form. A third criterion adopted here is the trend of the $H(\mathbf{r})$ along the Ng–X BP, particularly at around the (3, −1) BCP.

The Ng–X bonds are, generally, distinguished into three types, namely A, B, or C. In *interactions of type A*, the atoms overlap all the contour lines of their $H^+(\mathbf{r})$ regions and part of the contour lines of their $H^-(\mathbf{r})$ regions, the bond appearing as a continuous region of negative $H(\mathbf{r})$, plunged in a zone of positive values. The interaction is topologically signed on the bond axis by a (3, +1) HCP, namely, a critical point of $H(\mathbf{r})$ [a space point where $\nabla H(\mathbf{r}) = 0$] of rank $\hat{r} = 3$ and signature $s = +1$ [at any HCP, $\hat{r}$ is the rank of the matrix given by the number of nonzero eigenvalues of the Hessian matrix of $H(\mathbf{r})$ and s is the summation of their signing numbers, conventionally assigned as −1 to a negative eigenvalue and as +1 to a positive eigenvalue]. The intrinsic strength of bonds of type A is also conveniently assayed in terms of bond degree (BD). Borrowing a concept introduced so far by Espinosa *et al.*,⁵⁵ this index is defined³⁶ by the following equation:

$$\text{BD} = -\frac{H(\text{HCP})}{\rho(\text{HCP})}, \quad (4)$$

where $H(\text{HCP})$ and $\rho(\text{HCP})$ are, respectively, $H(\mathbf{r})$ and $\rho(\mathbf{r})$ at the HCP. Some illustrative examples are FHeO^- , HArF , and XeF_2 . The 2D plots of $H(\mathbf{r})$, shown in Figs. 1(a) and 1(d) and in Fig. 2(a), clearly unravel type A of any He–F, He–O, Ar–H, Ar–F, and Xe–F bond, with the red dots marking the corresponding (3, +1) HCP. The assignment is reinforced by examining $H(\mathbf{r})$ along the BP. For any He–F, He–O, Ar–H, Ar–F, and Xe–F bond, the function is negative for a long stretch of the BP, and particularly at around the BCP, it follows the featuring trends shown in Figs. 1(b), 1(c), 1(e), and 1(f) and in Fig. 2(b), namely, a concave-shape that includes a local maximum at the position of the (3, +1) HCP (note that this point is, generally, not coincident with the BCP, marked in the graphs by the vertical lines). The BD of the various bonds, calculated as 0.015 hartree e^{-1} for He–F, 0.849 hartree e^{-1} for He–O, 0.884 hartree e^{-1} for Ar–H, 0.228 hartree e^{-1} for Ar–F, and 0.524 hartree e^{-1} for Xe–F, clearly tells interactions of different strength. As best discussed in the subsequent paragraph, contacts of type A are, typically, covalent bonds or non-covalent bonds featuring a certain degree of electron sharing.

In *interactions of type B*, the $H^-(\mathbf{r})$ region of Ng is, again, overlapped with the $H^-(\mathbf{r})$ region of X. However, at variance with bonds

of type A, the corresponding HCPs are of variable signature and, generally, fall out of the bond axis. In the internuclear region, particularly along the BP, these bonds are best caught as the contact between a $H^-(\mathbf{r})$ region, to which mainly contribute the negative contour lines of Ng, and a $H^+(\mathbf{r})$ region, to which mainly contribute the positive contour lines of X. At around the BCP, $H(\mathbf{r})$ can take on different signs, and the various possible combinations are used here to distinguish the bonds into B-loose (B^l) or B-tight (B^t). A bond is B^l if $H(\mathbf{r})$ is positive at both the Ng and X sides of the BCP, the employed notation being $H^+(\text{Ng})\text{--}H^+(\text{X})$. A bond is, instead, B^t if $H(\mathbf{r})$ is negative at both the Ng and X sides [$H^-(\text{Ng})\text{--}H^-(\text{X})$] or of opposite sign at the two sides [$H^-(\text{Ng})\text{--}H^+(\text{X})$ or $H^+(\text{Ng})\text{--}H^-(\text{X})$]. B^l or B^t bonds are typical of complexes between a Ng donor and a (more or less strong) X acceptor. Three illustrative examples are ArBeO , KrBeO , and HeBO^+ . The 2D plot of $H(\mathbf{r})$ of ArBeO , shown in Fig. 3(a), clearly shows the effective overlap between the $H^-(\mathbf{r})$ regions of Ar and BeO that occurs out of the bond axis, topologically signed by the HCPs marked with the red dots. At these points, the BD calculated by using Eq. (4) amounts to 0.178 hartree e^{-1} and is appreciably lower than those predicted for FHeO^- , HArF , and XeF_2 (*vide supra*). As shown in Fig. 2(b), along the Ar–Be BP, particularly at around the BCP, $H(\mathbf{r})$ is positive at both the Be and Ar sides, even though becoming definitely negative moving by only 0.033 a_0 from the BCP to Ar. The contact is, therefore, $H^+(\text{Ar})\text{--}H^+(\text{Be})$, and the Ar–BeO bond is overall assigned as B^l . When going to KrBeO , the 2D plot of the $H(\mathbf{r})$ [Fig. 3(c)] is qualitatively similar to that of ArBeO . However, as shown in Fig. 3(d), $H(\mathbf{r})$ is (nearly) null at the BCP (−0.0009 hartree a_0^{-3}), and positive/negative moving along the BP toward Be/Kr. This $H^-(\text{Kr})\text{--}H^+(\text{Be})$ contact thus unravels an interaction of incipient B^l type. The BD at the HCPs [the red dots of Fig. 3(d)], 0.223 hartree e^{-1} , is also higher than the one predicted for ArBeO . The He–B bond of HeBO^+ , is, instead, definitely assigned as B^t . The 2D plot of the $H(\mathbf{r})$ [Fig. 3(e)] shows, in fact, an extensive overlap of the H^- regions of He and BO^+ , and along the BP, at around the BCP, $H(\mathbf{r})$ is definitely negative at both the He and B sides [Fig. 2(f)]. The BD at the HCPs is also as high as 0.538 hartree e^{-1} .

In *interactions of type C*, Ng and the binding partner overlap only part of their $H^+(\mathbf{r})$ regions and their $H^-(\mathbf{r})$ regions remaining, instead, separated by a (more or less wide) region of positive $H(\mathbf{r})$. The bond is, thus, visually caught as two clearly distinguishable $H^-(\mathbf{r})$ regions, separated by a region of positive values of $H(\mathbf{r})$. Similar to the interactions of type B, when $H(\mathbf{r})$ along the Ng–X BP is positive at both sides of the BCP [$H^+(\text{Ng})\text{--}H^+(\text{X})$ contact], the bond is assigned as C-loose (C^l). When, instead, along the BP, the function is negative at both sides of the BCP [$H^-(\text{Ng})\text{--}H^-(\text{X})$] or of opposite sign [$H^-(\text{Ng})\text{--}H^+(\text{X})$ or $H^+(\text{Ng})\text{--}H^-(\text{X})$], the bond is C-tight (C^t). Four illustrative examples are ArKr , $\text{He}(\text{H}_3\text{O}^+)$, KrMgO , and $\text{XeF}_2\text{--CO}$. The 2D plot of $H(\mathbf{r})$ of ArKr [Fig. 4(a)] clearly shows the $H^-(\mathbf{r})$ regions of Ar and Kr definitely separated by a wide region of positive $H(\mathbf{r})$. The function is also positive for a long stretch of the BP and passes through a local minimum at around the BCP [Fig. 4(b)]. The Ar–Kr bond is, therefore, assigned as C^l . In $\text{He}(\text{H}_3\text{O}^+)$, the $H^-(\mathbf{r})$ regions of He and H_3O^+ are, again, separated [Fig. 4(c)], and as shown in Fig. 4(d), along the He–H BP, $H(\mathbf{r})$ is positive at both sides of the BCP. The interaction is, therefore, again assigned as C^l , even though one notes the relatively little extension of

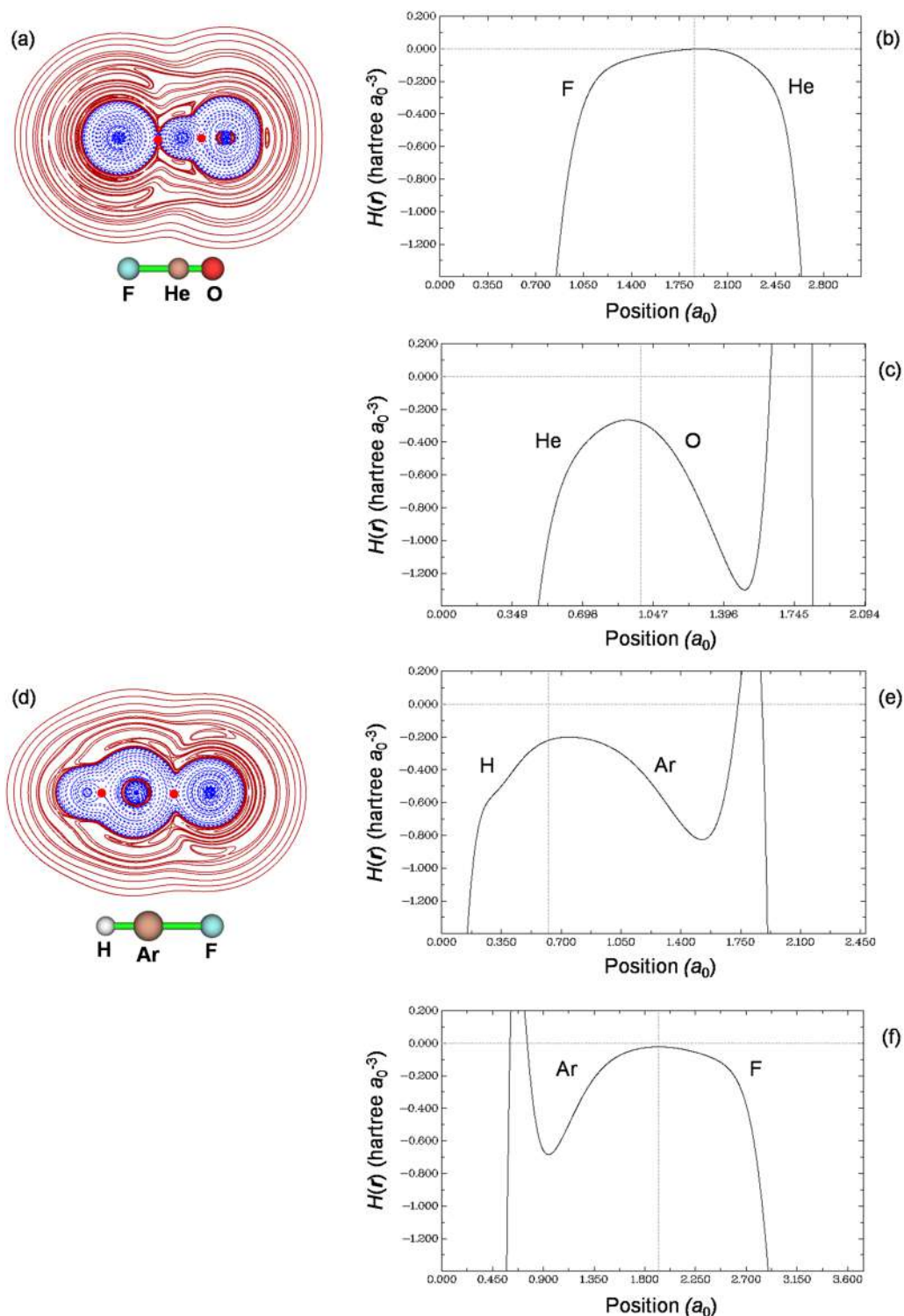


FIG. 1. Left: 2D plots of $H(r)$ in the symmetry planes of (a) FHeO⁻ and (d) HArF (brown solid and blue dashed lines correspond, respectively, to positive and negative values). The red dots mark the HCPs. Right: trend of $H(r)$ along the (b) F-He, (c) He-O, (e) H-Ar, and (f) Ar-F bond paths at around the corresponding BCP. The vertical lines mark the position of the BCP.

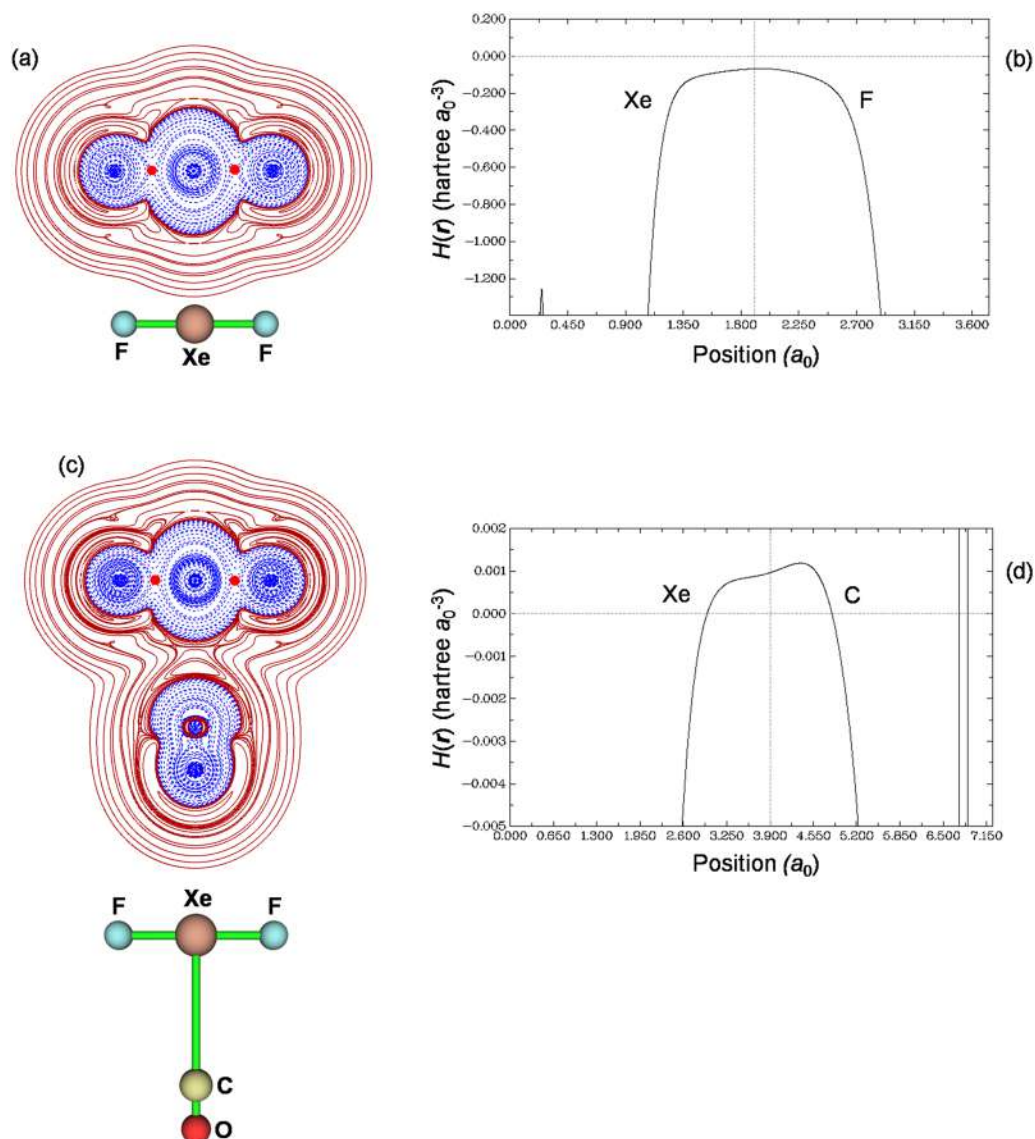


FIG. 2. Left: 2D plots of $H(r)$ in the symmetry planes of (a) XeF_2 and (c) $\text{XeF}_2\text{-CO}$ (brown solid and blue dashed lines correspond, respectively, to positive and negative values). The (red) dots mark the HCPs. Right: trend of $H(r)$ along the (b) Xe-F and (d) Xe-C bond paths at around the corresponding BCP. The vertical lines mark the position of the BCP.

the positive stretch on the H side. The Kr-Mg contact occurring in Kr-MgO, is, instead, assigned as $\text{C}^\dagger$. The 2D plot of $H(r)$ [Fig. 4(e)] shows, in fact, the separation of the $H^-(r)$ regions of Kr and MgO, but at around the BCP [Fig. 4(f)], the function is negative at both the Mg and Kr sides [$H^-(\text{Kr})$ - $H^-(\text{Mg})$].

Interactions of type C involving single Ng atoms, such as those occurring in ArKr, $\text{He}(\text{H}_3\text{O}^+)$, and KrMgO are conveniently assayed in terms of the *degree of polarization* of Ng, $\text{DoP}(\text{Ng})$. This index^{40,41,44} measures, in essence, the deformation of the $H^-(r)$ region of Ng arising from the interaction with X. It is, in particular, defined^{40,41,44} by the following equation:

$$\text{DoP}(\text{Ng}) = \frac{[R_{\text{Ng}}^-(\text{Ng} - \text{X}) - R_{\text{Ng}}^-] \times 100}{R_{\text{Ng}}^-}, \quad (5)$$

where $R_{\text{Ng}}^-(\text{Ng} - \text{X})$ is the radius of the $H^-(r)$ region of Ng along the axis formed by Ng and the Ng-X BCP and R_{Ng}^- is the radius of the $H^-(r)$ region of the free atom. The positive/negative sign of the DoP signals Ng atoms polarized toward/opposite to X, and the magnitude of the DoP is related to the extent of the polarization. For example, small DoP(Ar) and DoP(Kr) of ArKr, 0.15 and 0.079, respectively, are typical of dispersive contacts, while high and positive DoP(He)

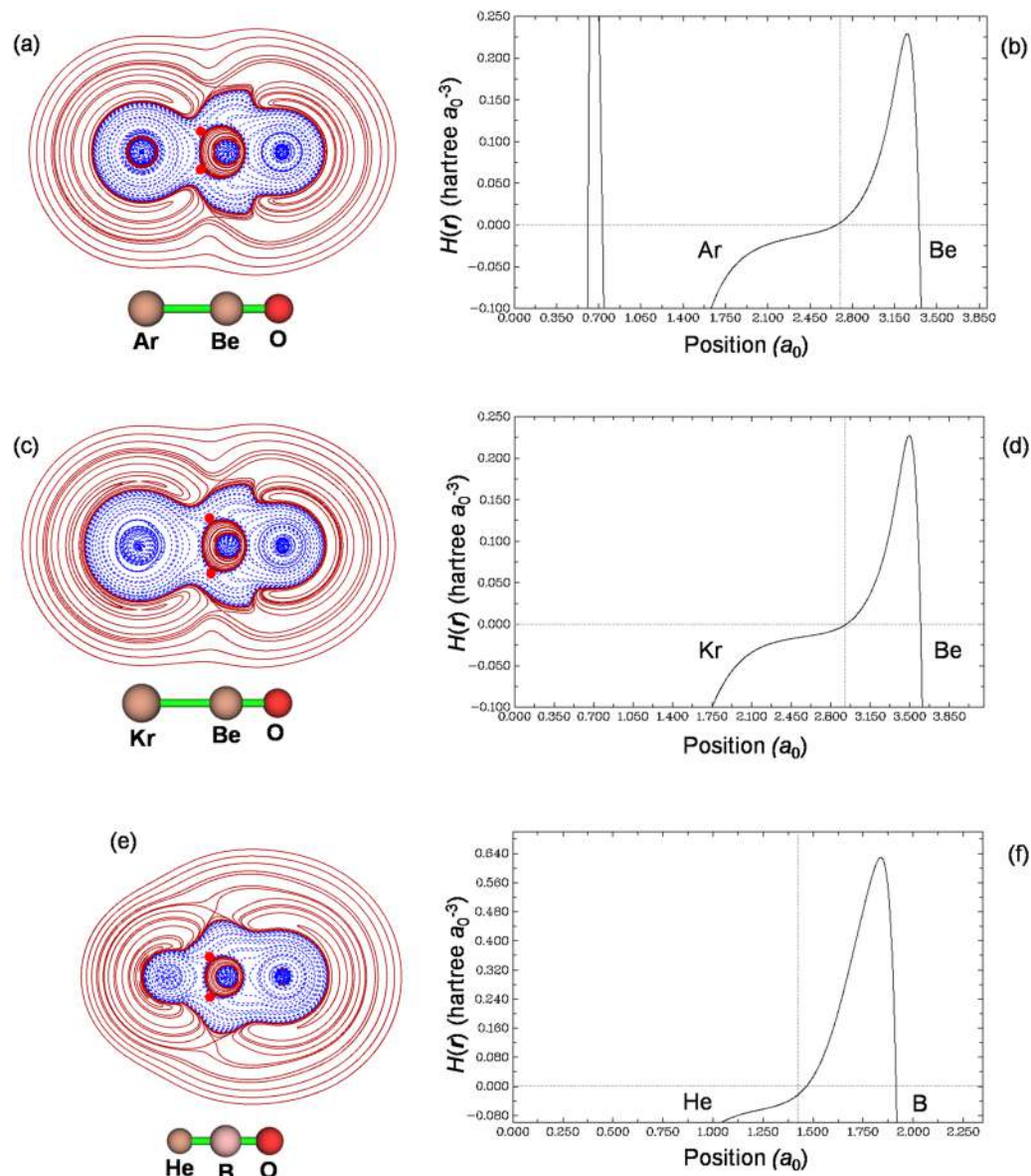


FIG. 3. Left: 2D plots of $H(r)$ in the symmetry planes of (a) ArBeO, (c) KrBeO, and (e) HeBO⁺ (brown solid and blue dashed lines correspond, respectively, to positive and negative values). The (red) dots mark the HCPs. Right: trend of $H(r)$ along the (b) Ar–Be, (d) Kr–Be, and (f) He–B bond paths at around the corresponding BCP. The vertical lines mark the position of the BCP.

of He(H₃O⁺), 6.80, and DoP(Kr) of KrBeO, 9.56, mirror the strong polarizing effect exerted by the ligands.

The Xe–C contact occurring in XeF₂–CO is an example of aerogen bond.^{56–63} As shown in Fig. 2(c), the $H^-(r)$ regions of XeF₂ and CO are separated by a wide region of positive $H(r)$. In addition, the function is positive for a long stretch of Xe–C path, and as shown in Fig. 2(d), at around the BCP, it is definitely positive at both the Xe and C sides. The bond is, therefore, assigned as C^l.

Once assigned as of type A, B^l/B^t, or C^l/C^t, any Ng–X contact is further assayed in terms of degree of covalency. This is best illustrated in the subsequent paragraph.

C. The role of covalency

The in-case role of covalency in Ng–X bonds is assayed by integrating $\rho(r)$ and $H(r)$ over the volume Ω_s enclosed by the

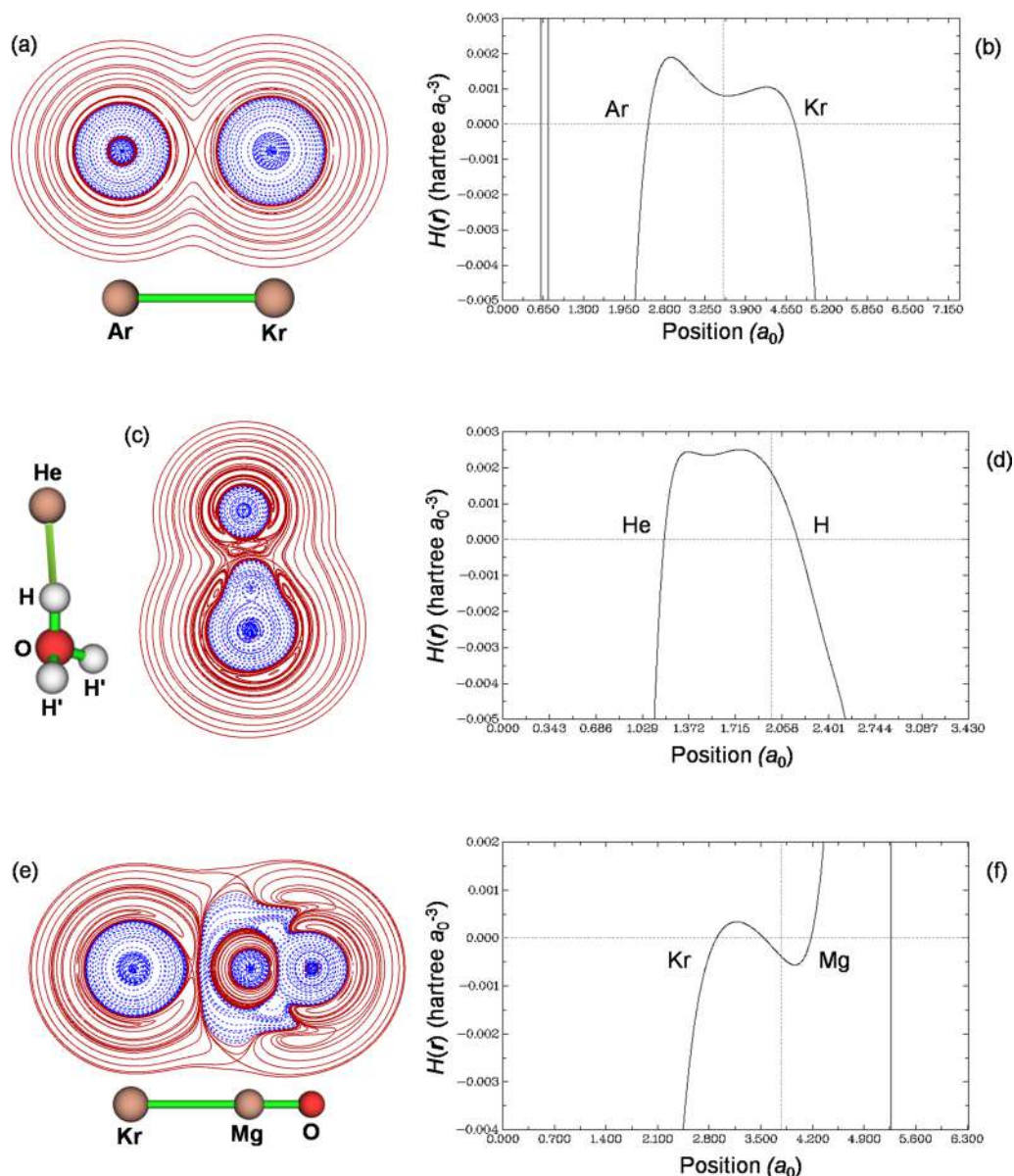


FIG. 4. Left: 2D plots of $H(r)$ in the symmetry planes of (a) ArKr, (c) He(H₂O⁺), and (e) KrMgO (brown solid and blue dashed lines correspond, respectively, to positive and negative values). Right: trend of $H(r)$ along the (b) Ar-Kr, (d) He-H, and (f) Kr-Mg bond paths at around the corresponding BCP. The vertical lines mark the position of the BCP.

RDG isosurface $s(r)$ associated with the bond (typically, the surface including the BCP). $s(r)$ is defined by the following equation:²¹

$$s(r) = \frac{|\nabla\rho(r)|}{2(3\pi^2)^{\frac{1}{3}} \times \rho(r)^{\frac{4}{3}}}, \quad (6)$$

and the integration is accomplished by producing an orthogonal grid of points that encloses the isosurface and applying the formula

$$P(\Omega_s) = \sum_{i(RDG < s)} P(r_i) d_x d_y d_z, \quad (7)$$

where $P(r_i)$ is the value of $\rho(r)$ or $H(r)$ at the grid point r_i and d_x , d_y , and d_z are the grid step sizes in the x , y , and z directions, respectively. The used values are $d_x = d_y = d_z = 0.025 a_0$, and the summation is carried out on all grid points r_i having $RDG < s$.

The interaction is, thus, assigned as covalent (Cov) if (i) the average electron density over Ω_s , $\rho_s(\text{ave})$ is $\geq 0.08 e a_0^{-3}$ and (ii)

the energy density over Ω_s , $H(\Omega_s)$, is, invariably, negative [the employed notation is $H(\Omega_s) = H^-$]. If one or both of these conditions are not fulfilled, the interaction is assigned as non-covalent (nCov) or partially covalent (pCov) according to the following criteria: (i) the interaction is nCov if, irrespective of $\rho_s(\text{ave})$, $H(\Omega_s)$ is, invariably, positive [$H(\Omega_s) = H^+$]; (ii) the interaction is pCov if (a) irrespective of $\rho_s(\text{ave})$, $H(\Omega_s)$ ranges from negative to positive [$H(\Omega_s) = H^{+/-}$ or $H^{-/+}$ if, on the average, $H(r)$ is positive or negative, respectively] or (b) $H(\Omega_s)$ is, invariably, negative (H^-), but $\rho_s(\text{ave}) < 0.08 e a_0^{-3}$.

The value of $s(r)$ on which to integrate $\rho(r)$ and $H(r)$ is chosen from the $s(r)$ vs $\text{sign}(\lambda_2) \times \rho(r)$ 2D plot so to capture the spike but only the spike associated with the interaction, without including tails of the atomic densities. Typical values are 0.1–0.2 for Cov bonds and 0.3–0.5 for pCov or nCov bonds. The results obtained, for example, for the exemplary species discussed in the previous paragraphs are quoted in Table I. The A bonds of FHeO^- are, clearly, different in nature. He–F is, in fact, assigned as pCov, with $\rho_s(\text{ave})$ being slightly lower than $0.08 e a_0^{-3}$ and $H(\Omega_s)$ being, partially, positive. The He–O contact is, instead, definitely covalent, with $\rho_s(\text{ave})$ as high as $0.2989 e a_0^{-3}$, and $H(\Omega_s)$ being invariably negative, and high in modulus. The A bonds of HArF are also both assigned as Cov, even though the appreciably different values of $\rho_s(\text{ave})$ (0.2215 vs $0.0957 e a_0^{-3}$) and $H_s(\text{ave/max/min})$ (see Table I) clearly confirm the different strength indicated by the different values of the BD (*vide supra*). $\rho_s(\text{ave})$ and $H_s(\text{ave/max/min})$ of the A bonds of XeF_2 are, also, typical of covalent contacts. As for the B^l or B^t bonds occurring in ArBeO , KrBeO , and HeBO^+ , the various indices clearly unravel a progressively increased degree of covalency. The Ar–Be, Kr–Be, and He–B bonds, are, in fact, assigned as, respectively, pCov($B^l/H^{+/-}$), pCov($B^t/H^{-/+}$), and Cov(B^t). The tight Kr–MgO contact is overall assigned as pCov(C^l/H^-), while ArKr , $\text{He}(\text{H}_3\text{O}^+)$, and $\text{XeF}_2\text{--CO}$ are all assigned as nCov from the invariably positive values of the

corresponding $H(\Omega_s)$. The relatively high value of $\rho_s(\text{ave})$ of $\text{He}(\text{H}_3\text{O}^+)$ mirrors, indeed, a major non-covalent contribution of ion-induced dipole character.

It is of interest to assay the Ng–X bonds listed in Table I in terms of the indices typically employed to classify the bonds within the AIM theory,¹⁷ namely, $\rho(r)$, the Laplacian of $\rho(r)$, $\nabla^2\rho(r)$, and $H(r)$ calculated at the BCP. The obtained data, listed in Table II, are generally well consistent with our Cov, pCov, or nCov assignments. Most of the Cov bonds feature, in fact, positive values of $\nabla^2\rho(\text{BCP})$, but $\rho(\text{BCP})$ is, invariably, rather high (between ~ 0.1 and $\sim 0.3 e a_0^{-3}$), and $H(\text{BCP})$ is definitely negative (between ~ -0.023 and ~ -0.28 hartree a_0^{-3}). This is, indeed, typical of covalent bonds. All the nCov assignments are also featuring the expected values of the AIM indices, namely, positive $\nabla^2\rho(\text{BCP})$ and $H(\text{BCP})$ and $\rho(\text{BCP})$ within $\sim 0.01 e a_0^{-3}$. In addition, the AIM indices of the pCov bonds are, consistently, in between those predicted for nCov and Cov: the $\rho(\text{BCP})$ ranges between ~ 0.01 and $0.08 e a_0^{-3}$, the $\nabla^2\rho(\text{BCP})$ is invariably positive, and the $H(\text{BCP})$ is slightly negative. The only exception is the positive $H(\text{BCP})$ of the Ar–BeO bond. Its pCov character arises, in fact, from values of $H(r)$ that are partially negative over the space enclosed by the 0.4 RDG isosurface: contribution that escapes the AIM analysis.

D. The procedure of bonding analysis

Our method of bonding analysis can be systematically applied according to the following procedure:

1. AIM analysis: The Ng–X contact is first ascertained by analyzing $\rho(r)$ and locating the corresponding bond path (BP) and bond critical point (BCP).
2. $H(r)$ analysis: The topological analysis of $H(r)$ of the whole molecule is then accomplished. This typically produces

TABLE I. MP2/aVTZ type and properties of the Ng–X bonds of FHeO^- , HArF , XeF_2 , ArBeO , KrBeO , HeBO^+ , ArKr , $\text{He}(\text{H}_3\text{O}^+)$, KrMgO , and $\text{XeF}_2\text{--CO}$ (see Figs. 1–4). $s(r)$ is the RDG isosurface at around the BCP; Ω_s is the volume (a_0^3) enclosed by $s(r)$; and $N(\Omega_s)$, $\rho_s(\text{ave})$, and $H_s(\text{ave/max/min})$ are, respectively, the total electronic charge (me), the average electron density ($e a_0^{-3}$), and the average, maximum, and minimum value of $H(r)$ (hartree a_0^{-3}) over Ω_s .

Species	Bond	Type	$s(r)$	Ω_s	$N(\Omega_s)$	$\rho_s(\text{ave})$	$H_s(\text{ave/max/min})$	$H(\Omega_s)^a$	BD ^b or DoP ^c	Assignment
FHeO^-	He–F	A	0.4	0.1292	9.17	0.0709	–0.0007/0.0033/–0.0103	$H^{-/+}$	0.015	pCov(A/ $H^{-/+}$)
	He–O	A	0.2	0.0666	19.9	0.2989	–0.2714/–0.1945/–0.4886	H^-	0.849	Cov(A)
HArF	Ar–H	A	0.2	0.1062	23.5	0.2215	–0.2328/–0.1692/–0.5860	H^-	0.884	Cov(A)
	Ar–F	A	0.2	0.0580	5.55	0.0957	–0.0205/–0.0163/–0.0248	H^-	0.228	Cov(A)
XeF_2	Xe–F	A	0.2	0.1531	18.7	0.1218	–0.0613/–0.0498/–0.0743	H^-	0.524	Cov(A)
ArBeO	Ar–Be	B^l	0.4	0.0819	2.47	0.0302	0.0012/0.0086/–0.0046	$H^{+/-}$	0.178	pCov($B^l/H^{+/-}$)
KrBeO	Kr–Be	B^t	0.4	0.1480	4.53	0.0306	–0.0024/0.0072/–0.0086	$H^{-/+}$	0.223	pCov($B^t/H^{-/+}$)
HeBO^+	He–B	B^t	0.2	0.0082	0.76	0.0925	–0.0243/–0.0107/–0.0353	H^-	0.538	Cov(B^t)
ArKr	Ar–Kr	C^l	0.4	0.1124	0.34	0.0030	0.0008/0.0008/0.0007	H^+	0.15 (Ar)/0.079 (Kr)	nCov(C^l)
$\text{He}(\text{H}_3\text{O}^+)$	He–H	C^l	0.4	0.0323	0.38	0.0118	0.0019/0.0022/0.0014	H^+	6.80	nCov(C^l)
KrMgO	Kr–Mg	C^t	0.4	0.7731	4.76	0.0062	–0.0003/–0.0005/–0.0006	H^-	9.56	pCov(C^t/H^-)
$\text{XeF}_2\text{--CO}$	Xe–C	C^l	0.4	0.1584	0.68	0.0044	0.0009/0.0010/0.0009	H^+		nCov(C^l)

^aDepending on the sign of $H_s(\text{ave/max/min})$, $H(\Omega_s) = H^+$, $H^{+/-}$, $H^{-/+}$, or H^- .

^bFor bonds of type A, B^l or B^t , BD (hartree e^{-1}) at the HCP calculated by using Eq. (4).

^cFor monocoordinated complexes of type C^l or C^t , DoP calculated by using Eq. (5).

TABLE II. MP2/aVTZ electron density $\rho(r)$ ($e a_0^{-3}$), Laplacian of the electron density, $\nabla^2\rho(r)$ ($e a_0^{-5}$), and energy density $H(r)$ (hartree a_0^{-3}) of the Ng–X bonds of FHeO[−], HArF, XeF₂, ArBeO, KrBeO, HeBO⁺, ArKr, He(H₃O⁺), KrMgO, and XeF₂–CO (see Figs. 1–4) calculated at the corresponding BCP.

Species	Bond	Assignment	$\rho(\text{BCP})$	$\nabla^2\rho(\text{BCP})$	$H(\text{BCP})$
FHeO [−]	He–O	Cov(A)	0.3090	0.3700	−0.2809
HArf	Ar–H	Cov(A)	0.2233	−0.6355	−0.2206
XeF ₂	Xe–F	Cov(A)	0.1284	0.2710	−0.0682
HArf	Ar–F	Cov(A)	0.0993	0.3380	−0.0226
HeBO ⁺	He–B	Cov(B ^t)	0.0945	0.8331	−0.0231
FHeO [−]	He–F	pCov(A/H ^{−/+})	0.0772	0.3756	−0.0021
KrBeO	Kr–Be	pCov(B ^t /H ^{−/+})	0.0332	0.1869	−0.0009
ArBeO	Ar–Be	pCov(B ^t /H ^{+/−})	0.0324	0.2258	0.0029
KrMgO	Kr–Mg	pCov(C ^t /H [−])	0.0066	0.0078	−0.0004
ArKr	Ar–Kr	nCov(C ^t)	0.0032	0.0121	0.0008
He(H ₃ O ⁺)	He–H	nCov(C ^t)	0.0122	0.0572	0.0019
XeF ₂ –CO	Xe–C	nCov(C ^t)	0.0046	0.0152	0.0010

various critical points (HCPs) of rank 3 and signature −3, −1, +1, or +3. The corresponding contour lines are collected as the HCP lines.

- The HCP/STD contour lines: The HCP lines are, then, combined with a group of standard (STD) $H(r)$ contour lines, a recommended choice being the patterns $\pm k \times 10^n$ ($k = 0, 1, 2, 4, 8; n = -5$ to 6).
- The plotted $H(r)$: The HCP/STD lines are, then, plotted so to visually establish the topology A, B, or C of the interaction. 2D plots in suitable planes are, in general, sufficient, but 3D plots of $H(r)$ may also help the assignment.
- The $H(r)$ along the BP: $H(r)$ along the Ng–X BP, particularly at around the BCP, is, then, examined to confirm the interactions of type A and to distinguish between B^t or B^t and C^t or C^t according to the criteria given in Table III.
- The $s(r)$ vs $\text{sign}(\lambda_2) \times \rho(r)$ 2D plot: The $s(r)$ vs $\text{sign}(\lambda_2) \times \rho(r)$ 2D plot is then examined, particularly at around the BCP of the Ng–X bond, so as to choose the $s(r)$ isosurface to integrate $\rho(r)$ and $H(r)$ and assay the degree of covalency. A recommended choice is the maximum value of $s(r)$ that still avoids the contribution of the tails of the atomic densities.

- The role of covalency: The Ng–X bond is, then, assigned as Cov, pCov, or nCov according to the criteria summarized in Table IV [Ω_s is the volume enclosed by the $s(r)$ chosen in step 6, $\rho_s(\text{ave})$ is the average electron density over Ω_s , and $H(\Omega_s)$ is the energy density over Ω_s]. The results of this step are best accounted by quoting the size of Ω_s ; the total electronic charge over Ω_s , $N(\Omega_s)$, and $\rho_s(\text{ave})$; and the average, maximum, and minimum value of $H(r)$ over Ω_s , $H_s(\text{ave/max/min})$.
- The final assignment: The bond is, finally, assigned using the notations Cov(Type), pCov[Type/ $H(\Omega_s)$], or nCov(Type), for example, Cov(A), pCov(B^t/H^{−/+}), or nCov(C^t).

E. Further illustrative applications

1. Interactions of type A: The ArX⁺ ($X = \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$)

Our procedure of bonding analysis is applied here to some illustrative systems taken from the recent literature.

The isoelectronic Ar-containing cations ArR⁺ ($R = \text{CH}_3, \text{NH}_2, \text{OH}, \text{and F}$) in their singlet ground state were recently investigated by DFT and CCSD(T) calculations.⁵² The combined use of different techniques of bonding analysis unraveled that all the Ar–X

TABLE III. Criteria to assign the Ng–X bonds of type A, B, or C in terms of the sign of $H(r)$ at around the BCP.

Bond type	$H(r)$ at around the BCP	
	Ng side	X side
A	Negative	Negative
B ^t or C ^t	Positive	Positive
B ^t or C ^t	Negative	Negative
	Negative	Positive
	Negative	Negative

TABLE IV. Criteria to assign the Ng–X bonds in terms of covalency.

	$\rho_s(\text{ave})^a$	$H(\Omega_s)$	Notation
Cov	≥ 0.08	Invariably negative	H [−]
pCov	< 0.08	Invariably negative	H [−]
	Any value	From negative to positive	H ^{+/-} (positive on the average)
			H ^{-/+} (negative on the average)
nCov	Any value	Invariably positive	H ⁺

^a $e a_0^{-3}$.

bonds ($X = \text{C}, \text{N}, \text{O}, \text{and F}$) are, mainly, of covalent character. The degree of covalency, however, gradually increases when going from $\text{Ar}-\text{C}$ to $\text{Ar}-\text{F}$, and the bonding situation actually shifts from the $\text{Ar} \rightarrow \text{R}^+$ dative σ bond in ArCH_3^+ and ArNH_2^+ to the $\text{Ar}-\text{R}^+$ electron-sharing σ bond in ArOH^+ and ArF^+ . This gradual change of bonding character also emerges from our bonding analysis. As shown in Fig. 5, the 2D plots of $H(r)$ of four ArR^+ clearly unravel type A of any $\text{Ar}-\text{X}$ bond. The region of negative $H(r)$ is, indeed, quite wide, and the function is definitely negative for a long stretch of the BP, particularly at around the BCP. The quantitative data quoted in Table V suggest, however, that these contacts are different in nature. For ArCH_3^+ , for both sampled $s(r)$ (0.15 or 0.20), $H(\Omega_s)$ is negative (H^-), but $\rho_s(\text{ave})$, predicted at around $0.075 e a_0^{-3}$, is close to but still lower than the threshold of covalency ($0.08 e a_0^{-3}$). The $\text{Ar}-\text{C}$ contact is, therefore, assigned as $\text{pCov}(\text{A}/\text{H}^-)$, even though at the onset of covalency. When going to ArNH_2^+ , ArOH^+ , and ArF^+ , $H(\Omega_s)$ is, invariably, negative and $\rho_s(\text{ave})$ is, invariably, higher than $0.08 e a_0^{-3}$. The $\text{Ar}-\text{N}$, $\text{Ar}-\text{O}$, and $\text{Ar}-\text{F}$ bonds are, therefore, all assigned as $\text{Cov}(\text{A})$. Their degree of covalency is, however, different and increases in the order $\text{Ar}-\text{N} < \text{Ar}-\text{O} < \text{Ar}-\text{F}$. In fact, as shown in Table V, when going from ArNH_2^+ to ArF^+ , $H_s(\text{ave})$ decreases from $-0.0505 \text{ hartree } a_0^{-3}$ to $-0.1624 \text{ hartree } a_0^{-3}$ and $\rho_s(\text{ave})$ increases from $0.1234 e a_0^{-3}$ to $0.2275 e a_0^{-3}$. The change in the bonding character occurring when going from ArCH_3^+ to ArF^+ is also effectively caught in terms of BD, predicted as $0.337 \text{ hartree } e^{-1}$ for the $\text{Ar}-\text{C}$, $0.406 \text{ hartree } e^{-1}$ for the $\text{Ar}-\text{N}$, $0.522 \text{ hartree } e^{-1}$ for the $\text{Ar}-\text{O}$, and $0.639 \text{ hartree } e^{-1}$ for the $\text{Ar}-\text{F}$ bond.

2. Interactions of type B: The Be bonds of ArBeNR and KrBeNR ($R = \text{H}, \text{F}, \text{CH}_3$)

The beryllium bond (BeB) was first proposed in 2009 by Yáñez, Mó, and their co-workers, who explored the complexes between BeX_2 ($X = \text{H}, \text{F}, \text{Cl}, \text{OH}$) and different Lewis bases.⁶⁴ Since then, the BeB has been definitely included in the family of NCIs,^{65,66} and its nature and influence on other non-covalent contacts have been deeply investigated.^{67–75} The interaction arises from the σ - or π -hole^{76–81} existing at the Be atom of the Lewis acceptor, and with typical inorganic and organic Lewis donors, it is mainly driven by the electrostatic interaction. The complex may also be stabilized by polarization and dispersion, but these contributions are often

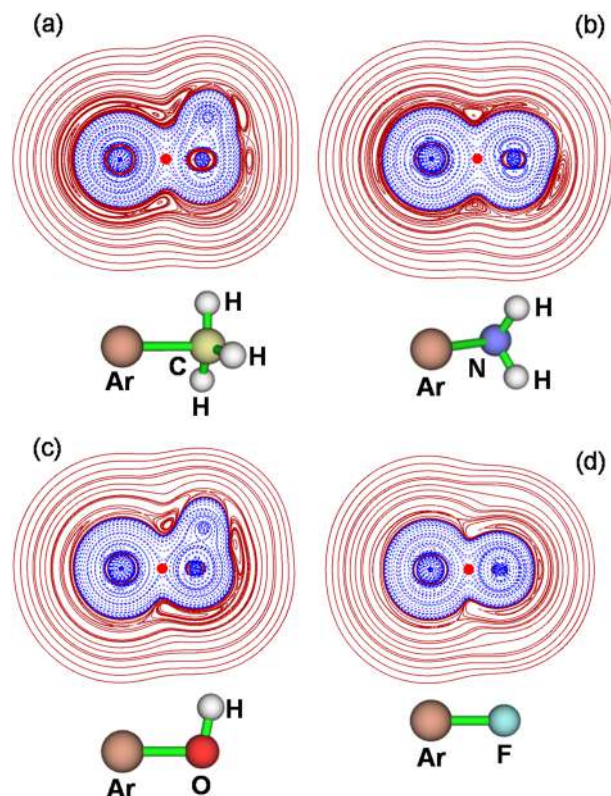


FIG. 5. 2D plots of $H(r)$ in the symmetry planes of (a) ArCH_3^+ , (b) ArNH_2^+ , (c) ArOH^+ , and (d) ArF^+ (brown solid and blue dashed lines correspond, respectively, to positive and negative values). The (red) dots mark the HCPs.

masked by the dominating role of the electrostatics. Enlightening information in this regard can be obtained by studying, in particular, complexes containing the Ng atoms. In these systems, in fact, the absence of permanent electric charges or multipoles on Ng reduces the contribution of the electrostatics, and this brings to light all the other binding components.¹² Working in this perspective, the complexes of $\text{He}-\text{Xe}$ with the prototypical BeNH , partly

TABLE V. MP2/aVTZ type and properties of the $\text{Ar}-\text{X}$ bonds ($X = \text{C}, \text{N}, \text{O}, \text{F}$) of ArCH_3^+ , ArNH_2^+ , ArOH^+ , and ArF^+ (see Fig. 5). $s(r)$ is the RDG isosurface at around the BCP; Ω_s is the volume (a_0^3) enclosed by $s(r)$; and $N(\Omega_s)$, $\rho_s(\text{ave})$, and $H_s(\text{ave}/\text{max}/\text{min})$ are, respectively, the total electronic charge (me), the average electron density ($e a_0^{-3}$), and the average, maximum, and minimum value of $H(r)$ (hartree a_0^{-3}) over Ω_s .

Species	Bond	Type	$s(r)$	Ω_s	$N(\Omega_s)$	$\rho_s(\text{ave})$	$H_s(\text{ave}/\text{max}/\text{min})$	$H(\Omega_s)$	BD ^a	Assignment
ArCH_3^+	$\text{Ar}-\text{C}$	A	0.15	0.1111	8.47	0.0762	$-0.0332/-0.0250/-0.0522$	H^-	0.337	$\text{pCov}(\text{A}/\text{H}^-)$
			0.20	0.2445	18.4	0.0754	$-0.0326/-0.0204/-0.0712$	H^-		$\text{pCov}(\text{A}/\text{H}^-)$
ArNH_2^+	$\text{Ar}-\text{N}$	A	0.15	0.0637	7.85	0.1234	$-0.0505/-0.0438/-0.0636$	H^-	0.406	$\text{Cov}(\text{A})$
			0.20	0.1516	18.4	0.1212	$-0.0491/-0.0388/-0.0722$	H^-		$\text{Cov}(\text{A})$
ArOH^+	$\text{Ar}-\text{O}$	A	0.15	0.0600	10.9	0.1824	$-0.0958/-0.0840/-0.1220$	H^-	0.522	$\text{Cov}(\text{A})$
			0.20	0.1433	25.7	0.1794	$-0.0941/-0.0746/-0.1370$	H^-		$\text{Cov}(\text{A})$
ArF^+	$\text{Ar}-\text{F}$	A	0.15	0.0605	13.8	0.2275	$-0.1624/-0.1367/-0.2379$	H^-	0.639	$\text{Cov}(\text{A})$

^aBD (hartree e^{-1}) at the (3, +1) HCP calculated by using Eq. (4).

investigated so far by two of us,⁸² were also recently revisited⁷⁴ in light of various techniques of bonding analysis. For any NgBeNH, the ELF analysis suggested that the polarization of each partner upon interaction has to be taken into account to properly describe the Coulombic interaction between the Ng atom and the beryllium σ -hole. Consistently, symmetry-adapted perturbation theory (SAPT)⁸³ confirmed the minor role (if any) of the electrostatics and unraveled the major contribution of the induction, typically four to five times larger than that of the dispersion. Based on these findings, we explored these bonding situations by our method of bonding analysis. We examined, in particular, exemplary ArBeNH and KrBeNH and also extended the study to their congeners ArBeNR and KrBeNR ($R = \text{F}, \text{CH}_3$), so as to taste the conceivable effects of the substituent R . The obtained results are given in Fig. 6 and Table VI. Consistent with stabilizing interactions of mainly inductive character, the 2D plots of $H(r)$ (Fig. 6) unravel the topology of type B of any Ar–BeNR and Kr–BeNR contact ($R = \text{H}, \text{F}$, and CH_3). The study of $H(r)$ at around the BCP also unraveled that any Ar–BeNR bond is of type B^1 , but the corresponding Kr–BeNR is of type B^t . This actually mirrors a different degree of covalency, predicted as, respectively, $H^{+/-}$ and $H^{-/+}$. Thus, the Kr–BeNR bond is tighter than any corresponding Ar–BeNR, and this is also confirmed by the BD at the HCP (see Table VI), predicted, for any R , to be appreciably higher for the Kr congener. One also notes from Table VI that when going from any Ar–BeNR to the corresponding Kr–BeNR, both Ω_s and $N(\Omega_s)$ appreciably increase. Their ratio $\rho_s(\text{ave})$ is, however, nearly constant for the six complexes and predicted at around $0.03 e a_0^{-3}$. This suggests caution when simply using the electron density as an index of bond strength. We finally note that, within the two series of the ArBeNR and KrBeNR, the various quantitative indices feature only minor changes. This suggests that, similar to the ArBeNH and KrBeNH, the major stabilizing component of the $-\text{F}$ and $-\text{CH}_3$ containing complexes is, indeed, the inductive one.

3. Interactions of type C: Probing the nature of aerogen bonds

The aerogen bond (or Ng bond, NgB), first highlighted by Bauzá and Frontera,^{56–58} can be outlined as the attractive interaction between an electron-rich atom or group of atoms and any element

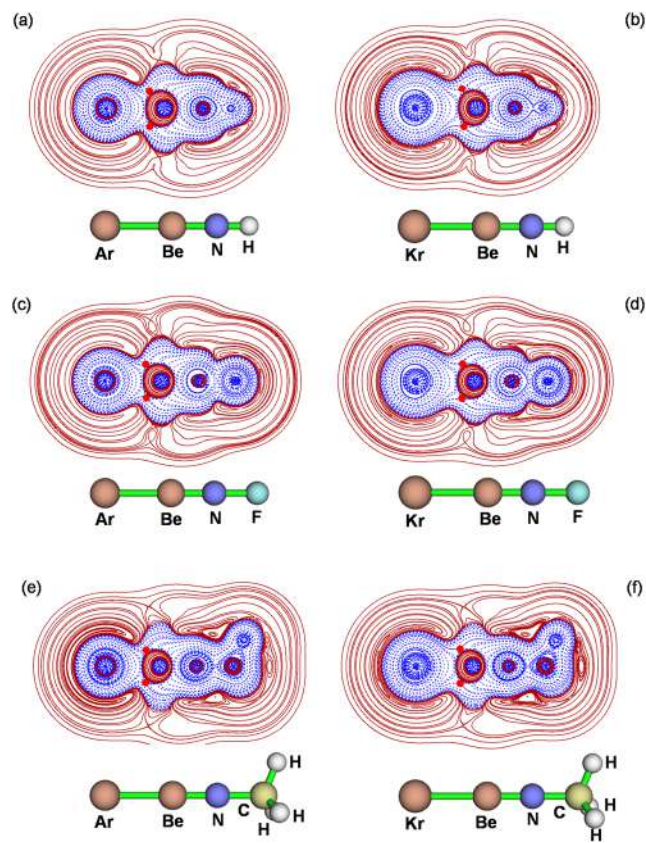


FIG. 6. 2D plots of $H(r)$ in the symmetry planes of (a) ArBeNH, (b) KrBeNH (c) ArBeNF, (d) KrBeNF, (e) ArBeNCH₃, and (f) KrBeNCH₃ (brown solid and blue dashed lines correspond, respectively, to positive and negative values). The (red) dots mark the HCPs.

of group 18 acting as an electron acceptor.^{59,60} The NgB governs, in particular, the architectures observed in the crystal structures of the xenon oxides and fluorides and of their complexes with various Lewis bases,⁶⁰ actually stabilized by interactions strictly analogous

TABLE VI. MP2/aVTZ type and properties of the Ar–Be and Kr–Be bonds of ArBeNR and KrBeNR ($R = \text{H}, \text{F}, \text{CH}_3$) (see Fig. 6). $s(r)$ is the RDG isosurface at around the BCP; Ω_s is the volume (a_0^3) enclosed by $s(r)$; and $N(\Omega_s)$, $\rho_s(\text{ave})$, and $H_s(\text{ave}/\text{max}/\text{min})$ are, respectively, the total electronic charge (me), the average electron density ($e a_0^{-3}$), and the average, maximum, and minimum value of $H(r)$ (hartree a_0^{-3}) over Ω_s .

Species	Bond	Type	$s(r)$	Ω_s	$N(\Omega_s)$	$\rho_s(\text{ave})$	$H_s(\text{ave}/\text{max}/\text{min})$	$H(\Omega_s)^a$	BD ^b	Assignment
ArBeNH	Ar–Be	B^1	0.4	0.1041	3.12	0.0300	0.0011/0.0084/–0.0048	$H^{+/-}$	0.198	pCov($B^1/H^{+/-}$)
ArBeNF	Ar–Be	B^1	0.4	0.1345	4.08	0.0303	0.0005/0.0086/–0.0051	$H^{+/-}$	0.212	pCov($B^1/H^{+/-}$)
ArBeNCH ₃	Ar–Be	B^1	0.4	0.1347	4.08	0.0303	0.0005/0.0101/–0.0047	$H^{+/-}$	0.200	pCov($B^1/H^{+/-}$)
KrBeNH	Kr–Be	B^t	0.4	0.1840	5.65	0.0307	–0.0028/0.0070/–0.0089	$H^{-/+}$	0.244	pCov($B^t/H^{-/+}$)
KrBeNF	Kr–Be	B^t	0.4	0.2418	7.54	0.0312	–0.0036/0.0073/–0.0095	$H^{-/+}$	0.261	pCov($B^t/H^{-/+}$)
KrBeNCH ₃	Kr–Be	B^t	0.4	0.2064	6.25	0.0303	–0.0027/0.0073/–0.0088	$H^{-/+}$	0.253	pCov($B^t/H^{-/+}$)

^a Depending on the sign of $H_s(\text{ave}/\text{max}/\text{min})$, $H(\Omega_s) = H^{+/-}$ or $H^{-/+}$.

^b BD (hartree e^{-1}) at the HCP falling out of the bond axis calculated by using Eq. (4).

to those occurring in other σ -hole and π -hole NCIs. Further insights into the NgB formed, in particular, by xenon fluorides were recently gained by Gomila and Frontera.⁸⁴ They performed, *inter alia*, theoretical calculations on the complexes of the neutral and cationic XeF_n ($n = 2, 4, 6$) and XeF_n^+ ($n = 3, 5$) with the exemplary ligands CO, HF, HCN, NH_3 , Br^- , and I^- . For the neutral XeF_n , the strength of the NgB typically increases when going from $n = 2$ to $n = 6$, and the bond, meanwhile, features an increased contribution of covalency (as signaled, in particular, by the AIM indices). It was also found that, for any donor, the strength of the NgB dramatically increases when going from XeF_n to XeF_n^+ , the role of covalency also becoming more pronounced. Stimulated by these findings, we decided to assay these systems by our adopted criteria. We thus extended the study of the exemplary XeF_2 -CO described in Sec. III B to the neutral and ionic congeners XeF_4 -CO, XeF_6 -CO, XeF_3^+ -CO, and XeF_5^+ -CO. The obtained results are given in Fig. 7 and in Table VII. The visual inspection of the 2D plots of $H(r)$ leaves no doubt on the clearly different character of the interactions occurring in the neutral and ionic species. Thus, similar to XeF_2 -CO (see Fig. 2), the graphs of XeF_4 -CO and XeF_6 -CO are clearly telling of Xe-C interactions of type C. Based on the values of $H(r)$ along the BP and on the invariably positive values of $H(\Omega_s)$, they are overall assigned as nCov($\text{C}^\dagger$). It is, however, possible to note from Table VII that the values of Ω_s , $N(\Omega_s)$, and $\rho_s(\text{ave})$ [nearly independent of the chosen value of $s(r)$] progressively increase when going from $n = 2$ to $n = 6$. This is, indeed, consistent with the theoretical prediction of a NgB increasing in the same order from 1.1 to 3.5 kcal mol⁻¹.⁸⁴ The 2D graphs of XeF_3^+ -CO and XeF_5^+ -CO and the values of the $H(r)$ along the BP are, instead, typical of interactions of type A. The $H^-(r)$ regions of XeF_3^+ or XeF_5^+ and CO are, in fact, overlapped, and at around the BCP, $H(r)$ is negative at both the Xe and C sides. However, as clearly eye-caught by inspecting Fig. 7, the degree of overlapping of the $H^-(r)$ regions, quite extensive in XeF_3^+ -CO, is only incipient in XeF_5^+ -CO. This mirrors quite different values of the BD at the HCP of the Xe-C bond, predicted as 0.135 hartree a_0^{-3} for XeF_3^+ -CO and only 0.004 hartree a_0^{-3} for XeF_5^+ -CO. As a matter of fact, for the two species, any bond index is significantly different in value, invariably telling of a tighter interaction occurring in the

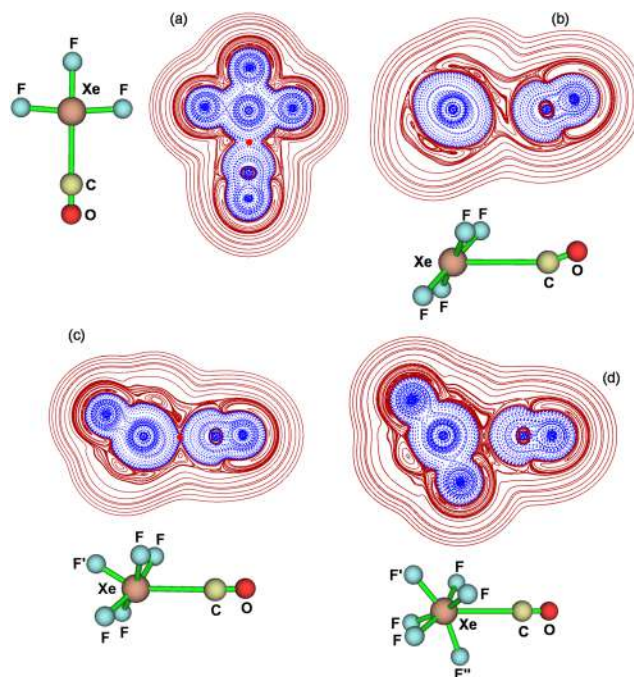


FIG. 7. 2D plots of $H(r)$ of (a) XeF_3^+ -CO, (b) XeF_4 -CO (Xe-C-O plane), (c) XeF_5^+ -CO (F' -Xe-C-O plane), and (d) XeF_6 -CO (F' - F'' -Xe-C-O plane) (brown solid and blue dashed lines correspond, respectively, to positive and negative values). In (a) and (c), the red dots mark the HCPs.

XeF_3^+ -CO. The contribution of covalency is also consistently different, the Xe-C bond being assigned as pCov(A/H^-) in XeF_3^+ -CO and pCov($\text{A}/\text{H}^{+/-}$) in XeF_5^+ -CO. The strength of the NgB occurring in the two species is, indeed, appreciably different and predicted as ~ 17 kcal mol⁻¹ for XeF_3^+ -CO and ~ 11 kcal mol⁻¹ for XeF_5^+ -CO.⁴¹ In any case, both these values are significantly higher than those predicted for the neutral XeF_n -CO (*vide supra*).

TABLE VII. MP2/aVTZ type and properties of the Xe-C bonds of XeF_n -CO ($n = 2, 4, 6$) and XeF_n^+ -CO ($n = 3, 5$) (see Fig. 7). $s(r)$ is the RDG isosurface at around the BCP; Ω_s is the volume (a_0^3) enclosed by $s(r)$; and $N(\Omega_s)$, $\rho_s(\text{ave})$, and $H_s(\text{ave}/\text{max}/\text{min})$ are, respectively, the total electronic charge (me), the average electron density ($e a_0^{-3}$), and the average, maximum, and minimum value of $H(r)$ (hartree a_0^{-3}) over Ω_s .

Species	Bond	Type	$s(r)$	Ω_s	$N(\Omega_s)$	$\rho_s(\text{ave})$	$H_s(\text{ave}/\text{max}/\text{min})$	$H(\Omega_s)^a$	Assignment
XeF_2 -CO	Xe-C	$\text{C}^\dagger$	0.4	0.1584	0.68	0.0044	0.0009/0.0010/0.0009	H^+	nCov($\text{C}^\dagger$)
			0.5	0.2985	1.29	0.0043	0.0009/0.0010/0.0008	H^+	nCov($\text{C}^\dagger$)
XeF_3^+ -CO	Xe-C	A	0.4	0.7457	27.0	0.0362	-0.0042/ - 0.0015/ - 0.0081	H^-	pCov(A/H^-)
			0.5	1.4737	51.7	0.0351	-0.0040/ - 0.0005/ - 0.0110	H^-	pCov(A/H^-)
XeF_4 -CO	Xe-C	$\text{C}^\dagger$	0.4	0.6555	3.86	0.0059	0.0011/0.0013/0.0007	H^+	nCov($\text{C}^\dagger$)
			0.5	1.1824	6.81	0.0058	0.0011/0.0013/0.0007	H^+	nCov($\text{C}^\dagger$)
XeF_5^+ -CO	Xe-C	A	0.5	1.1090	19.9	0.0180	0.0004/0.0014/ - 0.0014	$\text{H}^{+/-}$	pCov($\text{A}/\text{H}^{+/-}$)
XeF_6 -CO	Xe-C	$\text{C}^\dagger$	0.4	1.0431	11.6	0.0111	0.0012/0.0013/0.0008	H^+	nCov($\text{C}^\dagger$)
			0.5	1.9941	21.3	0.0107	0.0012/0.0014/0.0006	H^+	nCov($\text{C}^\dagger$)

^a Depending on the sign of $H_s(\text{ave}/\text{max}/\text{min})$, $H(\Omega_s) = \text{H}^+$, $\text{H}^{+/-}$, or H^- .

IV. CONCLUDING REMARKS

One of the most fascinating aspects of noble-gas chemistry is the variety of occurring bonding motifs, ranging from weakest non-covalent contacts to strong covalent bonds. The procedure of bonding analysis accounted in this article effectively describes all these diverse situations. The main analyzed function is $H(r)$. In the practice of the AIM theory, this function is, typically, employed as a “point” index, used to catch, through its sign at the BCP, covalent contributions that escape other indices. In our taken approach, we examine three more general aspects of $H(r)$, namely, the shape of its plotted form, the topology, and the value that the function takes along the AIM bond path associated with the bond, particularly at around the BCP. This allows for the systematic classification of any Ng–X bond, described also in terms of numerical indices defined in connection with the various types of bonds. To hopefully encourage the wide application of our method, we also reported a detailed step-by-step procedure, aimed at also best clarifying the practical use of our taken approach. We actually plan to implement a code that automatically accomplishes the various demanded steps.

At least, in principle, our employed method is applicable to any chemical bond. As a matter of fact, preliminary tests performed on covalent, ionic, and non-covalent species of elements other than the noble gases confirm this expectation. We will, therefore, go on to explore the potential of $H(r)$ to comprehensively describe the nature of the chemical bond at large. In this context, it will be, certainly, of interest to make comparisons with the results obtained, in particular, by methods that rely on perspectives different from quantum chemical topology. This could contribute to the still active debate concerning the strength and limitations of QTAIM and other related approaches and to further explore the expectedly effective complementary use of different methodologies of bonding analysis.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for (I) the full Cartesian coordinates of the presently investigated species and (II) three additional figures.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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