Noncovalent Complexes of the Noble-Gas Atoms: Analyzing the Transition from Physical to Chemical Interactions

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The bonding character of the noncovalent complexes of the noble-gas (Ng) atoms ranges from nearly purely dispersive contacts to interactions featuring appreciable contributions of induction and charge transfer. In this study, we discuss a new quantitative index that seems peculiarly informative about these diverse bonding situations. This index was termed as the degree of polarization (DoP) of Ng, as it measures, in essence, the Ng polarization promoted by the binding partner. The definition of the DoP(Ng) relies on the analysis of the local electron energy density $H(r)$, and its physical meaning was best appreciated by studying also the charge-displacement function and the molecular electrostatic potential of the investigated benchmark species, that include nearly 60 Ngs complexes of different bonding character. The DoP(Ng) appears of general applicability, and is also positively correlated with other bonding character indices. © 2019 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.26010

Introduction

Noncovalent interactions (NCIs) involving noble-gas atoms (Ng) have attracted, over the years, unceasing experimental and theoretical interest.[1] The most recent advance is the aerogen bond, first highlighted by Bauzá and Frontera[2–4] to designate a noncovalent contact between a covalently bonded atom of group 18 (particularly Kr and Xe) acting as a Lewis acid and any entity able to act as an electron donor. Supported also by the theoretical calculations, they recognized, in particular, that the architectures observed in the crystal structures of compounds such as XeO3, XeOF2, and XeF4 actually arise from specific interactions strictly analogous, for example, to the halogen, chalcogen, pnictogen, and tetral bond.[5] Subsequent studies[6–8] actually confirmed the major role in the aerogen bond of the $\sigma$-hole and the $\pi$-hole[9–11] existing at the Ng atoms of the involved compounds. The Ng atoms are also able to form weakly bound complexes with neutral molecules (M), the Ng(M) being generally regarded as typical van der Waals molecules,[12,13] held together by the favorable balance between the long-range dispersive attraction and the short-range Pauli repulsion. The Ng atoms, however, while generally resistant to form true ionic or covalent bonds, sensibly respond to the in case polarization exerted by the ligands. Thus, even for complexes with nonpolar molecules, the binding energies may include not only inductive, but also charge transfer (CT) stabilizing components. The latter contribution is particularly relevant, as it marks the transition from a purely (or nearly purely) “physical” contact to a more specific “chemical” noncovalent bond. In particular, some of us recently ascertained[14–21] that the CT plays a major role in the complexes of the Ng atoms, particularly He, Ne, and Ar, with $\text{H}_2\text{O}$,[14–16] NH$_3$,[17] CCl$_4$,[18,19] and Cl$_2$.[20,21] These systems could be, actually, assigned as remarkable examples of “nascent” hydrogen and halogen bonds. These studies were conducted by molecular beam experiments able to probe the absolute scale of the Ng-M intermolecular potential, and theoretical calculations able to probe, inter alia, the role of the CT. The latter was, in particular, assayed by studying the charge-displacement (CD) function,[22] that is peculiarly informative about the fluxes of charge accompanying the formation of a complex from its free composing fragments. Particularly for the Ng($\text{H}_2\text{O}$), Ng(NH$_3$), Ng(CCl$_4$), and Ng(Cl$_2$), the CT unraveled especially relevant for certain configurations of the complex, namely, the H-coordinated isomer of Ng($\text{H}_2\text{O}$) and Ng(NH$_3$), the vertex isomer of the Ng(CCl$_4$), and the linear Ng(Cl$_2$). This stereospecificity was related to the anisotropy of the electronic distribution of the ligand, particularly to the $\sigma$-hole existing at the H atoms of H$_2$O and NH$_3$, and at the Cl atoms of CCl$_4$ and Cl$_2$ on the outer prolongation of the covalent bonds. Thus, when approaching the ligand in the direction collinear to these bonds, the Ng feels a reduced repulsive wall, and, due to the electrophilic character of the $\sigma$-hole, it is polarized up to the occurrence of the CT.

Stimulated by these findings, we focus here on the complexes of the Ng atoms with the hydrogen halides HX (X = F, Cl, Ne, and Ar, with $\text{H}_2\text{O}$,[14–16] NH$_3$,[17] CCl$_4$,[18,19] and Cl$_2$.[20,21] These systems could be, actually, assigned as remarkable examples of “nascent” hydrogen and halogen bonds. These studies were conducted by molecular beam experiments able to probe the absolute scale of the Ng-M intermolecular potential, and theoretical calculations able to probe, inter alia, the role of the CT. The latter was, in particular, assayed by studying the charge-displacement (CD) function,[22] that is peculiarly informative about the fluxes of charge accompanying the formation of a complex from its free composing fragments. Particularly for the Ng($\text{H}_2\text{O}$), Ng(NH$_3$), Ng(CCl$_4$), and Ng(Cl$_2$), the CT unraveled especially relevant for certain configurations of the complex, namely, the H-coordinated isomer of Ng($\text{H}_2\text{O}$) and Ng(NH$_3$), the vertex isomer of the Ng(CCl$_4$), and the linear Ng(Cl$_2$). This stereospecificity was related to the anisotropy of the electronic distribution of the ligand, particularly to the $\sigma$-hole existing at the H atoms of H$_2$O and NH$_3$, and at the Cl atoms of CCl$_4$ and Cl$_2$ on the outer prolongation of the covalent bonds. Thus, when approaching the ligand in the direction collinear to these bonds, the Ng feels a reduced repulsive wall, and, due to the electrophilic character of the $\sigma$-hole, it is polarized up to the occurrence of the CT.

Stimulated by these findings, we focus here on the complexes of the Ng atoms with the hydrogen halides HX (X = F, Cl,
Br, I) that feature a σ-hole at both the H and X atoms, whose magnitude depends on X, and spans a range of several tens of kilocalories per mol.[23] We examined, in particular, two families of exemplary species, namely, the Ng(HF) (Ng = He-Xe), and the Ar(HX) (X = Cl, Br, I). The nature of their bond was deeply analyzed through the study of the NCI indices,[24] the CD function,[22] and the local electron energy density \( \rho(r) \),[25] and lead to define a new quantitative index, the Ng degree of polarization \( \text{DoP}(\text{Ng}) \), that signals, in essence, the mode and the extent of the Ng polarization promoted by the binding partner. The bonding analysis was also extended to other prototypical systems, such as the NgAr, Ng(Na\(^+\)), Ng(F\(^-\)), Ng(H\(_2\)), and Ng(N\(_2\)) (linear and T-shaped configurations), and the obtained results confirmed the viable use of the DoP(Ng) to distinguish between bonding situations ranging from purely (or nearly purely) dispersive contacts to interactions featuring inductive components, up to the occurrence of the CT. We discuss here the major features of the DoP(Ng), its physical origin, and its relationships with other bonding character indices.

### Methodology

We carried out single point energy calculations with the coupled cluster method with inclusion of single and double substitutions (CCSD)[26] together with the Dunning’s correlation consistent triple-zeta basis set (aug-cc-polarized valence triple zeta (pVTZ))[27–31] The I and Xe atoms were treated by the Stuttgart/Cologne small-core (28 electrons), scalar-relativistic effective core potential (ECP-28)[32] and the jointly designed aug-cc-pVTZ-PP basis set.[32] The adopted geometrical parameters, listed in Table 1 as a reference, were taken from the literature.[33–35] These highly accurate data are based on flexible analytical potentials fitting theoretical energies obtained by symmetry-adapted perturbation theory (SAPT) or CCSD(T) calculations performed with large basis sets, typically the aug-cc-pVnZ (n = D, T, Q, 5) with mid-bond functions, or experimental quantities such as spectroscopic absorptions, differential cross sections for collisional excitations, and bulk properties, often taken in combination (multiproperty fits). All the investigated species are true minima on the surface, the only exceptions being the T-shaped NgH\(_2\)) and the linear NgN\(_2\)). These complexes were anyhow included in the bonding analysis.

The computed wavefunctions were analyzed with the Multwf5 program[36] using the wfn or wfx files generated by the Gaussian 03[37] or the Gaussian 09[38] (in the CCSD calculations, the convergence criteria were \( 10^{-10} E_h \) on the energy and \( 10^{-6} \) on the change in the cluster amplitudes). The two-dimensional (2D) plots of the \( \rho(r) \) were as well produced with the Multwf5, and include the standard contour lines belonging to the patterns \( \pm k \times 10^9 \) \( (k = 1, 2, 4, 8; n = -5/6) \), and the contour lines corresponding to the critical points specifically located by the topological analysis of the \( \text{H}(\text{r}) \). The Multwf5 was also employed to perform the atoms in molecules (AIMs)[39] and the NCI[24] analysis. The three-dimensional (3D) NCI plots were produced with the visual molecular dynamics (VMD) program.[40] All the quantities are expressed in atomic units [for \( \rho(\text{r}) \), 1 \( a_0 \) = 1 e \( a_0^{-3} \) = 6.7483 eÅ\(^{-3}\); for \( \text{H}(\text{r}) \), 1 \( a_0 \) = 1 \( E_h \) \( a_0^{-3} \) = 6.7483 \( E_h \) Å\(^{-3}\)]

The analysis of the CD function

The CD analysis of the Ng(HF) (Ng = He–Xe) and Ar(HX) (X = Cl, Br, I) was carried out at the CCSD level of theory with the aug-cc-pVTZ and aug-cc-pVQZ basis sets using a parallel version of MOLPRO.[61] In general, the CD function[22] relies on the following expression:

\[
\Delta \rho(\text{r}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x,y,z) dx dy dz
\]

\( \Delta \rho \) being the difference between the electron density of the complex, and that of the isolated constituting fragments, placed at their positions in the complex. At each point along z (identified here, in particular, as the X-H-Ng or H-X-Ng axis, \textit{vide infra}), \( \Delta \rho \) measures the net electron charge that, upon formation of the complex, flows from right to left across the plane perpendicular to z. Thus, a negative \( \Delta \rho \) corresponds to a flux of charge from left to right. This provides a concise, but insightful snapshot, of the whole electron cloud rearrangement arising as the consequence of the intermolecular potential effect. The evaluation of \( \Delta \rho(z) \) along this axis joining the two interacting species is immediately helpful for a qualitative assessment of occurrence and extent of CT. In particular, the curve obviously suggests CT when it is appreciably different from zero, and it does not change sign in the region between the fragments. On the other hand, the CT may be uncertain (both in magnitude and in direction) if the curve crosses zero in the same region. When the CT takes place, it is convenient to come up with a definite numerical estimate, which can be done by taking the value of the CD curve at a specific point between the fragments. According to our previous studies,[14–21,62,63] we choose to separate the fragments and to extract the CT at the so-called isodensity boundary, that is, at the point along z where the electron densities of the noninteracting fragments become equal.

The analysis of the \( \text{H}(\text{r}) \)

The \( \text{H}(\text{r}) \) is the sum of the kinetic energy density \( G(\text{r}) \), and the potential energy density \( V(\text{r}) \). The former is always positive, and the latter is always negative. Thus, at variance with the \( \rho(\text{r}) \), that is invariably positive, the \( \text{H}(\text{r}) \) may be positive, negative, or null. In particular, in the inner atomic regions, \( G(\text{r}) \) is, typically, lower than \( |V(\text{r})| \), and \( \text{H}(\text{r}) \) is negative. On the other hand, in the outer atomic regions, \( G(\text{r}) \) is, typically, higher than \( |V(\text{r})| \), and \( \text{H}(\text{r}) \) is positive. The \( \text{H}(\text{r}) \) is also minimum (most negative) at the nucleus, and progressively increases (sometimes being locally null or positive), until becoming definitely null at a distance, indicated here as \( R \), that is typical of each atom. For \( R > R \), the \( \text{H}(\text{r}) \) is positive, and becomes vanishingly small at the largest distances, passing through a point of maximum. In essence, as best discussed in our previous study,[25] the \( \text{H}(\text{r}) \) partitions the atomic space in two well-recognizable regions, namely an inner one of negative values (that sometimes encloses tiny inner subregion[s] of positive values), indicated here as \( H^-(\text{r}) \), and an outer one of positive values (that sometimes encloses tiny inner subregion[s] of negative values), indicated here as \( H^+(\text{r}) \). The boundary of these two regions falls at a distance \( R \), that is typical of each atom; at this distance, \( H^+(\text{r}) = 0 \). Interestingly, when two atoms form a chemical bond, their \( H^-(\text{r}) \) and \( H^+(\text{r}) \) regions combine in modes that signal the character of the interaction. In particular, when forming a covalent...
bond, the atoms overlap all the contour lines of their $H^+(r)$ regions, and part of the contour lines of their inner $H^-(r)$ regions, the bond appearing as a continuous region of negative values of $H(r)$, plunged in a zone of positive values. The interaction is typically signed by a $(3,+1)$ critical point of the $H(r)$, indicated here as HCP, falling on the bond axis. On the other hand, when undergoing a NCI, the involved atoms or molecules overlap only part of their $H^+(r)$ regions, their $H^-(r)$ regions remaining, instead, not overlapped. The bond thus appears as two clearly distinguishable regions of negative values of $H(r)$, separate by a more or less wide region of positive values. At variance with the covalent bonds, the noncovalent contacts are not generally signed by a HCP. This arises, essentially, from the bell shape of the $H(r)$ in the outer $H^+(r)$ region (further details are given in Ref. [25]), that sometimes prevents the formation of a true HCP along the bond axis. In cases like these, we sign the interaction by including, in the plotted form of the $H(r)$, the bond critical point (BCP) located from the AIM analysis. In fact, based on the study of diverse noncovalent species, including numerous Ng complexes, we ascertained that, when located analytically, the HCP falling on the axis of a noncovalent bond is quite close to the corresponding BCP.

**Results and Discussion**

**Bonding character of the Ng(HX): The role of the CT**

The complexes of the Ng atoms with the hydrogen halides HX are generally stabilized mainly by dispersive interactions. However, particularly for the X-H-Ng systems, both theory and experiments have long suggested the appreciable role of inductive and even CT bonding components.\[^{13,36,64}\] The noncovalent character of the Ng(HX) was first confirmed by the results of the NCI analysis. The latter relies\[^{24}\] on the study of the reduced density gradient $s(r)$ defined by the equation

\[
s(r) = \frac{1}{2\langle \mathbf{\nabla}^2 \rho(r) \rangle^\lambda} \frac{\nabla^2 \rho(r)}{\rho(r)}
\]

and the sign($\lambda_2)$ of $\rho(r)$, $\lambda_2$ being the second eigenvalue ($\lambda_1 < \lambda_2 < \lambda_3$) of the Hessian matrix of $\rho(r)$. Thus, for any Ng(HX), the 2D plot of the $s(r)$ versus the sign($\lambda_2)$ of $\rho(r)$ featured only one spike at the low density region, corresponding to the noncovalent contact between Ng and HX. The bonding region best emerged by examining the 3D plots of the isosurfaces of the $s(r)$ (fixed as 0.5 au), colored by the sign($\lambda_2)$ of $\rho(r)$ that progressively increases from blue ($\sim 0.05$ au) to red (0.05). As shown in Figure 1 for the six exemplary He(HF), Xe(HF), and Ar(HCl), a disk-shaped green area invariably appears between the two interacting fragments.

In these regions, the sign($\lambda_2)$ of $\rho(r)$ ranges between $-0.0015$ and $-0.010$ au, and values like these are generally suggestive of interactions dominated by the dispersion. It was, however, possible to note quantitative differences among the various complexes. Thus, for the F-H-Ng (Ng = He-Xe), the sign($\lambda_2)$ of $\rho(r)$ ranges between $-0.0025$ and $-0.010$ au, but these two limits

| | F-H-Ng | Ref. | H-F-Ng | Ref. |
|---|---|---|---|---|
| He | 1.7499/4.3199 | [33] | 1.7499/5.5804 | [33] |
| Ne | 1.7329/4.4673 | [34] | 1.7329/5.7240 | [34] |
| Ar | 1.7329/4.8849 | [35] | 1.7329/6.2739 | [35] |
| Kr | 1.7329/5.0040 | [36] | 1.7329/6.4383 | [36] |
| Xe | 1.7329/5.3630 | [36] | 1.7329/6.7822 | [36] |
| Cl | 2.4377/5.2270 | [37] | 2.4377/6.8295 | [37] |
| Br | 2.6721/5.2969 | [38] | 2.6721/6.9032 | [38] |
| I | 3.0406/5.4869 | [39] | 3.0406/7.1375 | [39] |

Table 1. Bond distances ($\alpha_0$) of the presently investigated Ng complexes.

[a] R(H-H) = 1.4494 $\alpha_0$.
[b] R(N-N) = 1.40 $\alpha_0$.
[c] R(Ng-H) of the linear isomer.
[d] R(Ng-center of mass of H$_2$) of the T-shaped isomer.
[e] R(Ng(N)-N) of the linear isomer.
[f] R(Ng-center of mass of N$_2$) of the T-shaped isomer.
increase to $-0.0015$ and $-0.0045$ au on going to the H-F-Ng. In addition, for any Ng, the sign($\lambda_2(\rho(r))$ of the F-H-Ng is invariably more negative than that of the corresponding H-F-Ng. Similar differences were also noticed when comparing any X-H-Ar ($X = Cl, Br, I$) with the corresponding H-X-Ar. As a matter of fact, based also on the results obtained from the other techniques of bonding analysis (vide infra), these differences actually mirror the different roles of induction and CT in the stabilization of the various Ng(HX). The role of the CT was, in particular, assayed by exploring the CD function. The obtained results are shown in Figures 2 and 3, and quoted in Tables 2 and 3.

We first discuss the Ng(HF). For a more detailed illustration in the Ar case, Figure 2a also shows the 3D contour plots of the electron density difference between the complex and the non-interacting fragments. One first notes that, in the F-H-Ar configuration, the HF pronouncedly polarizes the spherical cloud of Ar, which undergoes a depletion/accumulation in the region opposite/toward HF. A visible amount of charge rearrangement is also present on the HF moiety. Especially significant, moreover, is the fact that, in the F-H-Ar configuration, the CD function is distinctly positive everywhere in the molecular region, thus providing evidence for the occurrence of a net CT in the direction from Ar toward HF. On the other hand, for the H-F-Ar configuration, the changes in the charge density are remarkably different, with less pronounced fluctuations, and an inverted polarization at the Ar center. The CD function is negative at the Ar site, indicating a charge polarization in the direction opposite to that seen in the F-H-Ar case. The curve approaches zero in the interfragment region, and a negligible CT from HF to Ar is, therefore, surmised. As shown in Figures 2b and 2c, the same conclusions hold for the other F-H-Ng and H-F-Ng. Any F-H-Ng features, in fact, a CT from Ng toward HF, and the transferred charge (quantitatively estimated as the $\Delta q$ value at the "isodensity boundary," vide supra) amounts (see Table 2) to $0.97$ me (He), $1.84$ me (Ne), $4.69$ me (Ar), $7.24$ me (Kr), and $9.23$ me (Xe). As shown in Table 2, these values remain, essentially, unchanged at the CCSD/aug-cc-pVQZ level of theory. The inverted polarization at the Ng center is, instead, the major feature of any H-F-Ng, with no contribution of CT.

The CD curves of the Ar(HX) ($X = Cl, Br, I$) (see Fig. 3) clearly indicate that the Ar spherical cloud of any X-H-Ar and H-X-Ar undergoes depletion/accumulation in the region opposite/toward HX, thus suggesting a Ar atom invariably polarized toward the ligand. It is, however, possible to note quantitative differences on going from $X = Cl$ to $X = I$. Thus, the H-Cl-Ar (Fig. 3a) features a modest charge polarization of Ar toward Cl, that increases on going to HBr (Fig. 3b), and HI (Fig. 3c). Indeed, the H-Cl-Ar CD pattern shows
The comparison of F-H-Ar with the X-H-Ar (X = Cl, Br, I) indicates the contribution of CT that increases by increasing the polarizability of Ng, the Ng atom is polarized opposite to the ligand. Thus, even if Br (2.82 me) > I (2.32 me), a tiny charge rearrangement, together with a change of sign in the intermolecular region. This suggests inductive bonding components, but the role of the CT, if present, is difficult to ascertain and is, presumably, minor. The CD curves of H-Br-Ar and H-I-Ar show still modest charge rearrangements, but they are invariably distinctly positive in the intermolecular region, and support the occurrence of a CT from Ar to HBr/Hi, that is quantitatively estimated (see Table 3) as 0.69 and 1.66 me, respectively, for H-Br-Ar and H-I-Ar. The CD curves of the X-H-Ar (X = Cl, Br, I) show the same pattern described for F-H-Ar (vide supra), and clearly unravel a more pronounced contribution of the CT. In any case, the amount of transferred charge decreases in the order F (4.69 me) > Cl (2.97 me) > Br (2.82 me) > I (2.32 me).

Overall, the study of the CD function unraveled that, in any H-F-Ng, the Ng atom is polarized opposite to the ligand. Thus, even if including inductive components, the interaction is assigned as “physical” in nature. On the other hand, any F-H-Ng features an appreciable contribution of CT that increases by increasing the polarizability of Ng. The comparison of F-H-Ar with the X-H-Ar (X = Cl, Br, I) indicates also that the CT decreases by decreasing the electronegativity of X. On the other hand, while relatively minor for the H-Cl-Ar, the CT progressively increases on going to H-Br-Ar and H-I-Ar. Once placed in the context of the analysis of the H(r), described in the subsequent paragraph, these trends decisively contributed to unravel the presently proposed index of bonding character.

The H(r) of the Ng(HX): Definition and properties of the DoP(Ng)

As shown in the previous study,[25] the analysis of the H(r) is informative about diverse types of bonding motifs, including those typically occurring in Ng compounds. Figures 4 and 5 show, in particular, the plotted H(r) of the Ng(HF) (Ng = He–Xe) and Ar(HX) (X = Cl, Br, I).

These graphs invariably confirm the noncovalent character of these complexes suggested by the NCI analysis. The H(r) regions of both Ng and HX are, in fact, perfectly closed, and separated by a wide region of positive values of H(r). All the covalent H–X bonds are also signed by an HCP falling on the bond axis. The various

### Table 2. Data obtained from the analysis of the CD function, the H(r), and the ρ(r) of the linear Ng(HF). All distances R are in au.

| CD | H(r) | ρ(r) |
|----|------|------|
| R(CT)[a] | CT[b] | RNG-BCP | DoP(Ng)[c] | R(BCP)[d] | ρ(BCP)[e] | V(r)(BCP)[f] | H(BCP)[g] | MEP(BCP)[h] |
| F-H-He | 2.3735 | 0.97 (1.75) | 1.1314 | 1.50 | 2.3951 | 0.0031 | 0.01754 | 0.00129 | 81.1 |
| F-H-Ar | 2.6910 | 1.84 (1.50) | 1.5470 | 1.28 | 2.0680 | 0.0048 | 0.02945 | 0.00122 | 92.6 |
| F-H-Ar | 3.2219 | 4.69 (4.78) | 2.4116 | 3.40 | 3.2033 | 0.0072 | 0.02965 | 0.00148 | 102 |
| F-H-Kr | 3.4535 | 7.24 (7.22) | 2.7912 | 5.48 | 3.3728 | 0.0088 | 0.03104 | 0.00113 | 107 |
| F-H-Xe | 3.7378 | 9.23 (8.86) | 3.2256 | 6.88 | 3.6933 | 0.0086 | 0.02559 | 0.00077 | 103 |
| H-F-He | 2.5379 | −0.11 (−0.10) | 1.1104 | 0.386 | 2.5346 | 0.0018 | 0.01100 | 0.00078 | −17.6 |
| H-F-Ne | 2.8516 | −0.15 (−0.10) | 1.5246 | 0.190 | 2.8501 | 0.0029 | 0.01631 | 0.00080 | −17.6 |
| H-F-Ar | 3.4771 | −1.21 (−1.19) | 2.3188 | 0.575 | 3.4308 | 0.0034 | 0.01703 | 0.00101 | −13.8 |
| H-F-Kr | 3.7171 | −2.12 (−1.90) | 2.6187 | −1.04 | 3.6337 | 0.0039 | 0.01843 | 0.00106 | −11.8 |
| H-F-Xe | 4.0421 | −3.03 (−2.95) | 2.9714 | −1.54 | 3.9583 | 0.0039 | 0.01646 | 0.00087 | −10.0 |

(a) Distance from Ng where the CT was evaluated.
(b) CT (me) at R(CT); in parenthesis values computed with the aug-cc-pVQZ basis set.
(c) Defined by eq. (3).
(d) Distance of the BCP from Ng.
(e) Electron density (e a₀⁻¹) at the BCP.
(f) Laplacian of the electron density (e a₀⁻³) at the BCP.
(g) Energy density (hartree a₀⁻¹) at the BCP.
(h) Molecular electrostatic potential (kcal mol⁻¹) at the BCP.

### Table 3. Data obtained from the analysis of the CD function, the H(r), and the ρ(r) of the linear Ar(HX). All distances R are in au.

| CD | H(r) | ρ(r) |
|----|------|------|
| R(CT)[a] | CT[b] | RNG-BCP | DoP(Ar)[c] | R(BCP)[d] | ρ(BCP)[e] | V(r)(BCP)[f] | H(BCP)[g] | MEP(BCP)[h] |
| F-H-Ar | 3.2219 | 4.69 | 2.4116 | 3.40 | 3.2033 | 0.0072 | 0.01754 | 0.00129 | 81.1 |
| C-H-Ar | 3.2995 | 2.97 | 2.3808 | 2.08 | 3.2945 | 0.0057 | 0.02206 | 0.00122 | 92.6 |
| Br-H-Ar | 3.2938 | 2.82 | 2.3744 | 1.81 | 3.3034 | 0.0056 | 0.02115 | 0.00116 | 56.5 |
| I-H-Ar | 3.3524 | 2.32 | 2.3652 | 1.41 | 3.3529 | 0.0050 | 0.01813 | 0.00101 | 42.5 |
| H-F-He | 3.4771 | −1.21 | 2.3188 | −0.575 | 3.4308 | 0.0034 | 0.01703 | 0.00101 | −13.8 |
| H-F-Ne | 3.4658 | 0.18 | 2.3433 | 0.476 | 3.4589 | 0.0036 | 0.01644 | 0.00113 | 17.7 |
| H-F-Ar | 3.4072 | 0.69 | 2.3514 | 0.823 | 3.4091 | 0.0042 | 0.01813 | 0.00116 | 27.1 |
| H-F-Kr | 3.7369 | 1.66 | 2.3598 | 1.18 | 3.4131 | 0.0044 | 0.01725 | 0.00103 | 36.9 |

(a) Distance from Ar were the CT was evaluated.
(b) CT (me) at R(CT).
(c) Defined by eq. (3).
(d) Distance of the BCP from Ar.
(e) Electron density (e a₀⁻¹) at the BCP.
(f) Laplacian of the electron density (e a₀⁻³) at the BCP.
(g) Energy density (hartree a₀⁻¹) at the BCP.
(h) Molecular electrostatic potential (kcal mol⁻¹) at the BCP.

[1] J. Comput. Chem. 2019, 40, 2318–2328.
Ng–H and Ng–X noncovalent contacts are, instead, not generally signed by such a HCP (vide supra). In any case, the AIM indices of the corresponding BCPs (the blue dots of Figs. 4 and 5) are typical of NCIs.[59] Thus (see Tables 2 and 3), the \( \rho(\text{BCP}) \) is invariably low (less than \( 0.0100 \text{ e} \text{a}^{-3} \)), the \( \nabla^2 \rho(\text{BCP}) \) is invariably positive, and, as shown in Figures 4 and 5, any BCP falls in the \( H^- (r) \) region. This makes transparent the fulfillment of a third AIM criterion of noncovalency, namely, a positive value of the \( \text{H}(\text{BCP}) \).

However, the most relevant information was gained by a deeper analysis of the \( H^- (r) \) region of the Ng atoms. For any free Ng, this region is spherical, and, as shown in Table 4, its size (measured by the value of \( R^- \)) progressively increases on going from He \( (R^- = 1.1147 \text{ a}_0) \) to Xe \( (R^- = 3.0180 \text{ a}_0) \). This essentially reflects the fact that, for any Ng, the \( H^- (r) \) region encloses the majority of the electronic charge (ca. 70% for He, and ca. 90–98% for the other congeners). These highest electron populations suggest also that the shape and size of the \( H^- (r) \) region of any Ng should be sensitive to the in case polarization exerted by the ligands.

Pursuing along this direction, we carefully examined the graphs plotted in Figures 4 and 5 and confirmed that the \( H^- (r) \) region of any Ng is, indeed, no more spherical. Rather, its radius depends on the direction, and, in particular, when compared with the \( R^- (\text{Ng}) \) of the free Ng, the most pronounced deviations occur along the Ng–H or Ng–X bond axis. We express this deviation by the equation

\[
\text{DoP}(\text{Ng}) = \frac{R_{\text{Ng-BCP}}(\text{Ng}) - R^- (\text{Ng})}{R^- (\text{Ng})} \times 100
\]

where \( R_{\text{Ng-BCP}}(\text{Ng}) \) is the radius of the \( H^- (r) \) region of Ng along the axis formed by Ng and the AIM BCP located on the Ng-M bond path, and \( R^- (\text{Ng}) \) is the radius of the \( H^- (r) \) region of the free Ng (see Table 4). The DoP(Ng) predicted, in particular, for the various Ng(HF) and Ar(HX) are quoted in Tables 2 and 3 (based on CCSD/aug-cc-pVQZ calculations performed for some exemplary helium complexes, these values are expected to undergo only minor changes if recalculated with basis sets larger than the aug-cc-pVTZ). The comparison with the data obtained from the study of the CD function (vide supra) supported the following considerations.

We first note that the sign of the DoP(Ng) is informative about the mode of polarization of Ng. Thus, as shown in Table 2, the DoP(Ng) of any H-F-Ng is negative, and ranges from \(-0.190 \text{ (H-F-Ne)} \) to \(-1.54 \text{ (H-F-Xe)} \). In these systems, in fact, as unraveled by the CD curves, the electronic cloud of Ng is shifted opposite to the ligand, and this produces a \( R_{\text{Ng-BCP}}(\text{Ng}) \) that is shorter than \( R^- (\text{Ng}) \). On the other hand, as shown in Table 3, with the only exception of H-F-Ar, the DoP(Ar) of any Ar(HX) is positive, and this is, again, consistent with the analysis of the CD function. In these complexes, in fact, the electronic cloud of Ar is shifted toward the ligand, and this produces a \( R_{\text{Ng-BCP}}(\text{Ng}) \) that is longer than \( R^- (\text{Ng}) \). Interestingly, as shown in Figure 6, a nearly linear correlation \( (r^2 = 0.994) \) does exist between the DoP(Ar) of the eight Ar(HX) \( (X = F, Cl, Br, I) \), and the \( \Delta \rho(\text{max}) \) derived from the CD curves (see Figs. 2 and 3). This suggests that the DoP(Ng) is a qualitative, but also a quantitative index of the Ng polarization exerted by the ligand. One also notes from Figure 7 that the DoP(Ar) of F-H-Ar and of the six Ar(HX) \( (X = Cl, Br, I) \) positively correlates with the corresponding CT as estimated from the study of the CD function.

![Figure 3](image-url)
The trend is, however, nonlinear, and this suggests that, once polarized toward HX, the charge transferred from Ar depends on the nature of the acceptor moiety. In any case, the graph indicates that, for a DoP(Ar) lower than a threshold value of about 0.5, no CT is expected. This suggests the conceivably general use of the DoP(Ng) to appreciate, for a Ng polarized toward the ligand, the transition from the “physical” to the “chemical” domain of the interaction.

The DoP(Ng) as an index of bonding character

To further validate the evidence obtained from the study of the Ng(HX), we calculated the DoP(Ng) of other numerous Ng complexes. We discuss here, in particular, the exemplary Ng(Na⁺) and Ng(F⁻), the linear and T-shaped Ng(H₂) and the Ng(N₂), and the NgAr, whose relevant data are quoted in Table 5.

In the Ng(Na⁺), the Ng atom is expected to be strongly polarized toward the ligand, and the interaction to be dominated by the induction, with the likely contribution of the CT. As a matter of fact, the DoP(Ng) of these complexes is invariably positive and large, ranging from 3.18 for Ne(Na⁺) up to 12.0 for XeNa⁺. We note, in particular, the DoP(Ar) of 8.82 predicted for the Ar(Na⁺), to be compared with a largest value of 3.4 predicted for the neutral Ar(HX) (see Table 3). On the other hand, the DoP(Ng) of any Ng(F⁻) is negative, and ranges from −1.56 for Ne(F⁻) to −8.69 for Xe(F⁻). This is fully consistent with an Ng atom that is, expectedly, strongly polarized opposite to the ligand. The Ng dimers are, instead, exemplary cases of nearly purely dispersive interactions. While the dispersion is also a mode of polarization, the ensuing effects on Ng are expected to be definitely minor than those arising from the induction. Consistently, as shown in Table 5, the DoP(Ng) of the NgAr arrives up to only 0.159 for Ng = Xe, and is typically lower.
than 0.1. Quite similar values were also obtained for all the other Ng\(_2\) and NgNg\(^0\). As for other complexes of expectedly dispersive
(or mainly dispersive) character, the DoP(Ng) generally resulted to be positive or negative, but typically between \(-0.2\) and 0.2. Exemplary in this regard are the slightly negative values predicted for the T-shaped Ng(H\(_2\)) (see Table 5). On the other hand, the DoP(Ng) of any linear Ng(H\(_2\)) is positive, and arrives up to about 0.5–0.6 for Ar(H\(_2\)) and Kr(H\(_2\)), thus suggesting the appreciable contribution of inductive bonding components. This is fully consistent, in particular, with the anisotropy of the Ar/H\(_2\) interaction potential and a more pronounced inductive character of the linear isomer that clearly emerged, in particular, since the first investigation by

\[ \text{Figure 5. } H(r) \text{ of the Ar(HX) (X = Cl, Br, I) plotted in planes containing the nuclei. The bond axis is z. Solid (brown) and dashed (blue) lines correspond, respectively, to positive and negative values. The (blue) dot signs the AIM BCP. [Color figure can be viewed at wileyonlinelibrary.com]} \]

\[ \text{Figure 6. } \text{DoP(Ar) of the Ar(HX) versus the corresponding } \Delta q(\text{max}). \text{[Color figure can be viewed at wileyonlinelibrary.com]} \]

Table 4. Values of the \(R^{-}(\alpha_0)\) of the Ng atoms, and occupation numbers \(N(e)\) of their \(H^{-}(r)\) regions. \(\rho(R^{-})\) is the electron density \((e\ a_0^{-3})\) at \(R^{-}\).

| Ng   | \(R^{-}(\alpha_0)\) | \(N(e)\) | \(\rho(R^{-})\) |
|------|---------------------|----------|-----------------|
| He   | 1.1147              | 1.39 (69.5) | 0.0677          |
| Ne   | 1.5275              | 8.97 (89.7) | 0.0741          |
| Ar   | 2.3322              | 16.89 (93.8) | 0.0269          |
| Kr   | 2.6463              | 34.86 (96.8) | 0.0199          |
| Xe   | 3.0180              | 52.75 (97.7) | 0.0151          |

[a] \(H^0 = R^{-}\) = 0.

[b] The value in parenthesis is the percentage with respect to the total number of electrons.
SAPT\(^{[66]}\) As for the linear and T-shaped Ng(N\(_2\)), their DoP(Ng) is, in general, relatively low in magnitude, thus confirming interactions dominated by the dispersion, with at most minor inductive components. In any case, likewise the Ng(H\(_2\)), the DoP(Ng) predicted for the linear and the T-shaped Ng(N\(_2\)) are of opposite sign, thus suggesting, again, an overall anisotropic interaction. However, ongoing from the Ng(H\(_2\)) to the Ng(N\(_2\)), the positive/negative sign of the DoP(Ng) of the linear/T-shaped isomers switches to a negative/positive one. This major difference is best understood by examining the physical origin of the DoP(Ng).

The physical origin of the DoP(Ng): The role of the molecular electrostatic potential

At first glance, the positive/negative sign of the DoP(Ng) of the Ng(Na\(^+\))/Ng(F\(^-\)) and F-H-Ng/H-F-Ng could mirror the positive/negative charge of Na\(^+\)/F\(^-\) and the atomic charges of HF, namely, positive on H, and negative on F. This interpretation, however, is not supported by the invariably positive DoP(Ar) predicted for any Ar(H\(_X\)) (X = Cl, Br, I), despite an invariably negative X of HX. In addition, the DoP(Ng) of the complexes with the apolar H\(_2\) and N\(_2\) should be, invariably, null. As a matter of fact, rather than mirroring the total atomic charges, the polarization effects signed by the DoP(Ng) are best related to the local electronic distributions of the ligands as mapped, in particular, by their molecular electrostatic potential (MEP).\(^{[67]}\) Exemplary in this regard are the Ng(HX) complexes. It is, in fact, well known that any HX features a \(\sigma\)-hole at both the H and the X atom.\(^{[23]}\) In particular, as shown in Table 6, irrespective of the mapped isodensity surface, the \(\sigma\)-holes of HCl, HBr, and HI are, invariably, positive. For HF, the \(\sigma\)-hole is positive at the H atom, but negative at the F one. Thus, if Ng is in contact with the H atom of any HX or with the halogen atom of HCl, HBr, and HI, it feels a locally positive charge, and is polarized toward the ligand. This produces a positive DoP(Ng). On the other hand, if Ng is bound to the F atom of HF, it feels a locally negative charge, and is polarized opposite to the ligand, the corresponding DoP(Ng) being negative. Likewise, the MEP of H\(_2\)/N\(_2\) is positive/negative on the outer elongation of the bond (corresponding to a \(\sigma\)-hole at the H

![Figure 7](image1.png)  
Figure 7. CT of the Ar(HX) versus the corresponding DoP(Ar). [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 8](image2.png)  
Figure 8. DoP(Ar) of the neutral argon complexes versus the corresponding MEP[BCP]. [Color figure can be viewed at wileyonlinelibrary.com]

### Table 5. DoP(Ng) and MEP(BCP) of the complexes of the Ng atoms with Na\(^+\), F\(^-\), H\(_2\), N\(_2\), and Ar.

| Ng | DoP(Ng) | MEP |
|----|---------|-----|
| Na\(^+\) | H | F |
| He | 7.29 | 278 | -2.14 |
| Ne | 3.18 | 284 | -1.56 |
| Ar | 8.82 | 276 | -5.14 |
| Kr | 11.0 | 270 | -7.60 |
| Xe | 12.0 | 262 | -8.69 |

### Table 6. \(V_{S,\text{Max}}\) and \(V_{S,\text{Min}}\) (kcal mol\(^{-1}\)) of the HX, H\(_2\), and N\(_2\) calculated at the isodensity surface \(\rho(l)\) (e \(a_0\)^{-3}).

| \(\rho(l)\) | H | F | Cl | H | Br | H | Br |
|-----------|-----|-----|-----|-----|-----|-----|-----|
| 0.0005    | 55.9 | -18.3 | 35.9 | 5.7 | 29.6 | 11.5 | 21.3 | 17.7 |
| 0.0010    | 69.1 | -19.4 | 44.3 | 9.3 | 36.9 | 16.1 | 27.1 | 23.4 |
| 0.0020    | 87.0 | -20.0 | 56.5 | 15.1 | 47.7 | 22.9 | 35.8 | 31.8 |
| 0.0030    | 100.8 | -19.7 | 66.2 | 19.8 | 56.5 | 28.6 | 43.1 | 38.8 |
| 0.0040    | 112.4 | -19.1 | 74.9 | 24.1 | 64.1 | 33.7 | 45.2 | 49.6 |

[a] Bond distances \(a_0\).
[b] Perpendicular to the bond.

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atom and to a $\sigma$-lump at the N atom) but negative/positive perpendicular to it. This explain the opposite pattern of the signs of the DoP(Ng) predicted for the linear and T-shaped Ng(H$_2$) and Ng(N$_2$) (vide supra). Interestingly, the DoP(Ng) appears to be also quantitatively correlated with the MEP. In this regard, rather than using the MEP of the free molecules projected on an arbitrarily chosen isodensity surface (e.g., the $\rho = 0.0010$ or 0.0020 e $\text{Å}^{-3}$ customarily taken in the literature), we are using here the MEP(BCP), namely, the MEP evaluated at the AIM BCP of the complex, taken as the contact point between Ng and the ligand. In particular, using the data quoted in Tables 3 and 5, Figure 8 shows the DoP(Ar) of the presently investigated Ar complexes with neutral ligands plotted versus the corresponding MEP(BCP). The correlation is nearly linear ($r^2 = 0.996$), and quantitatively expressed by the equation

$$\text{DoP(Ar)} = 0.0335 \times \text{MEP(BCP)} - 0.0524$$

(4)

(the slope and the correlation coefficient only slightly reduce, respectively, to 0.0326 kcal$^{-1}$ mol and 0.995 by fixing the intercept to zero). Using the data quoted in Tables 2 and 5, nearly linear correlations ($r^2$ between 0.994 and 0.998) were as well obtained for all the other Ng, the slopes (kcal$^{-1}$ mol) ranging between 0.0134 (Ng = Ne) and 0.0714 kcal$^{-1}$ mol (Ng = Xe).

Conclusions

In the present study, we obtained theoretical evidence for the DoP(Ng) as a d-dimensional quantitative index that is peculiarly informative about the bonding character of noncovalent Ng complexes. The DoP(Ng) signals, in essence, the mode and the extent of the Ng polarization promoted by the bonding partner, that are in turn related to the nature of the interaction. Thus, if the DoP(Ng) is negative, the Ng is polarized opposite to the ligand, and the complex may be stabilized by dispersion or induction, but no CT is expected. On the other hand, if the DoP(Ng) is positive, the Ng is polarized toward the ligand, and the bonding character may be purely (or nearly purely) dispersive, but may also include inductive components, up to the occurrence of the CT. These different scenarios can be distinguished based on the numerical value of the DoP(Ng) that progressively increases by increasing the role of the polarization and the CT. The physical interpretation of the DoP(Ng) as an index of polarization is also confirmed by its positive correlation with the MEP at the contact point between Ng and the binding partner. In essence, the local anisotropies of the electronic distribution of the ligand polarize the Ng atom in different modes and to different extents, and this determines the overall character of the ensuing interaction. Finally, as repeatedly highlighted in the literature,[1,2,3] even in the Coulombic $\sigma$-hole interpretation of NCIs, the inclusion of polarization is of major importance. The present results suggest that further insights in this regard could be obtained from the study of model complexes containing the Ng atoms.

Acknowledgments

This work was supported by the “Departments of Excellence-2018” Program (Dipartimenti di Eccellenza) of the Italian Ministry of Education, University and Research, DIBAF - Department of University of Tuscia, Project “Landscape 4.0 - food, well-being, and environment” and the DCBB - Department of Chemistry, Biology and Biotechnology of the University of Perugia, Project “AMIS: An Integrated Molecular Approach for the Sustainable Development.”

Keywords: bonding analysis · charge-displacement analysis · electron energy density · noble-gas chemistry · $\sigma$-hole

How to cite this article: S. Borocci, F. Grandinetti, N. Sanna, P. Antoniotti, F. Nunzi. J. Comput. Chem. 2019, 40, 2318–2328. DOI: 10.1002/jcc.26010
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Received: 12 April 2019
Revised: 1 June 2019
Accepted: 5 June 2019
Published online on 29 June 2019