

# Electronic Transmutation Concept: Is the Inverse Process Possible? An Evaluation of Main Group Compounds

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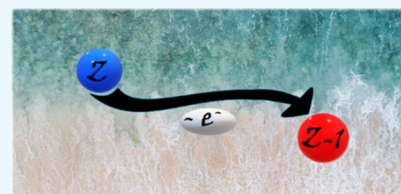


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**ABSTRACT:** The electronic transmutation (ET) concept states that when an element with atomic number  $Z$  gains an electron, it transmutes into a  $Z + 1$  element, leading to species that possess similar chemical bonding patterns and geometric structures regarding the original ( $Z + 1$ ) element. In this work, the opposite concept, that is, the inverse ET, is assessed. For this purpose, several main group compounds have been analyzed in terms of the adaptive natural density partitioning. The obtained results suggest that when an atom  $Z$  loses an electron, it transmutes into a  $Z - 1$  atom, acquiring its geometrical structure and bonding pattern.



## INTRODUCTION

In 2012, Olson and Boldyrev proposed the electronic transmutation (ET)<sup>1</sup> concept as an extension of the isoelectronic principle proposed by Gillis.<sup>2</sup> This concept states that when an element with atomic number  $Z$  gains an electron, it transmutes into a  $Z + 1$  element, leading to species that possess similar chemical bonding patterns and geometric structures regarding the original element. This concept has allowed several computational<sup>3–6</sup> and experimental studies.<sup>6–9</sup> The goal of this concept has been nicely reviewed by Boldyrev and co-workers,<sup>10</sup> where elements of the series 13, 14, and 15 have been transmuted into elements of the series 14, 15, and 16, respectively. The opposite case, that is, when an element with atomic number  $Z$  loses an electron, it acquires the geometry and bonding pattern of a  $Z - 1$  element, was mentioned in the original ET article; however, reports where this criterion has been used are scarce.

One way to test the ET concept is through known and well-characterized compounds. As an example, we have the case of  $\text{Li}_3\text{N}_3$  by Olson et al.,<sup>11</sup> where the  $\text{N}_3^{3-}$  unit of this compound is isoelectronic to ozone; in addition, it has a similar geometry and a bonding pattern consistent with the latter compound, so according to the authors, nitrogen has transmuted to oxygen when acquiring an electron.

Another class of interesting compounds is the boratabenzenes,<sup>12</sup> aromatic compounds with a  $\text{B}^-$  unit, so it could be stated that boron has transmuted into carbon.<sup>13</sup> These compounds have gone from being “chemical curiosities” to having a great variety of applications.<sup>14,15</sup> Additionally, polycyclic derivatives have been obtained such as boratanaphthalenes<sup>16</sup> and borataphenanthrenes.<sup>13,17</sup>

Some years ago, Goesten and co-workers<sup>18</sup> studied the electronic structure and chemical bond of  $\text{CsO}_4^+$  and concluded that this compound is reminiscent of  $\text{XeO}_4$  and also said that  $\text{Cs}^+$  resembles hypervalent Xe. On the other hand, small cations, like fluoronium<sup>19</sup> ( $\text{H}_2\text{F}^+$ ) and chloro-

onium<sup>20</sup> ( $\text{H}_2\text{Cl}^+$ ), are isoelectronic to  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , respectively, having geometries similar to the latter compounds with differences in bond lengths and angles of 0.01 Å for both compounds and 10.0 and 2.0° for  $\text{H}_2\text{F}^+/\text{H}_2\text{O}$  and  $\text{H}_2\text{Cl}^+/\text{H}_2\text{S}$ , respectively. Furthermore, their valence molecular orbitals (see Figure 1) are identical. In addition, aromatic systems such as pyridinium and pyrylium cations are isoelectronic to benzene and pyridine, respectively. The question that arises is: is it possible that N and O have inversely transmuted into C and N, respectively?

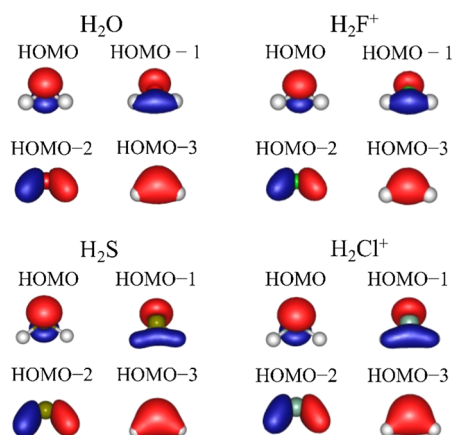


Figure 1. Valence molecular orbitals for  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{F}^+$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{Cl}^+$ .

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On the other hand, Islas et al.<sup>21</sup> have recently reported a series of isoelectronic analogues to the highly stable B<sub>12</sub><sup>22</sup> cluster, containing one and two C<sup>+</sup> units (as stated by Olson and Boldyrev in the original publication<sup>1</sup>); however, in the absence of a detailed analysis of the bonding pattern, it cannot be confirmed whether the C<sup>+</sup> units have transmuted to boron. Moreover, chemical bond pattern in Si<sub>4</sub><sup>2+</sup>, which is isoelectronic to Al<sub>4</sub><sup>2-</sup>, has not been analyzed in detail, but it was observed that both compounds have the same aromatic character according to Nguyen et al.'s results, and it has been postulated that when doped with C, this atom has a planar tetracoordinate geometry.<sup>23</sup>

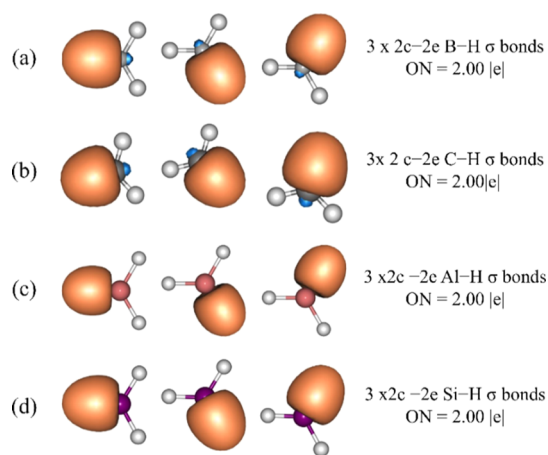
On the other hand, theoretical studies show that ArOH<sup>+</sup> and XeF<sup>+</sup> possess strong covalent Ar–O and Xe–F bonds.<sup>24,25</sup> These molecules are isoelectronic to well-characterized HOCl and IF, so they have been selected to investigate if Ar and Xe have been inversely transmuted into Cl and I, respectively. The aim of the present study is to assess the inverse ET concept in known and well-characterized compounds from the first periods of XIII to XVIII groups of the periodic table. For this purpose, the chemical bond has been analyzed using adaptive natural density partitioning<sup>26</sup> (AdNDP), a useful tool that allows a complete understanding of the chemical bond, which is a generalization of the natural bond orbital (NBO) method developed by Weinhold<sup>27</sup> and enables to recover Lewis characteristic 1c–2e and 2c–2e bonds and additionally allows the study of delocalized systems for an assignment of (anti)aromaticity by means of electron-counting rules.<sup>28</sup>

## COMPUTATIONAL DETAILS

Geometry optimizations were carried out using Gaussian16 B.01<sup>29</sup> package at the PBE0-D3<sup>30,31</sup>/def2-QZVP<sup>32</sup> level. Additionally, to ensure that we have a minimum in the potential energy surface (PES), vibrational calculations were performed at the same level (for the coordinates of the optimized systems, see Table S2). Chemical bonding analysis by means of AdNDP developed by Zubarev and Boldyrev<sup>26</sup> was performed through NBO 6.0<sup>33</sup> and Multiwfn<sup>34</sup> programs. Ring current strength calculations were performed for Al<sub>4</sub><sup>2-</sup> and Si<sub>4</sub><sup>2+</sup> using the AIMAll program.<sup>35</sup> Visualization of canonical and AdNDP orbitals was made using the Chemcraft software.<sup>36</sup>

## RESULTS AND DISCUSSION

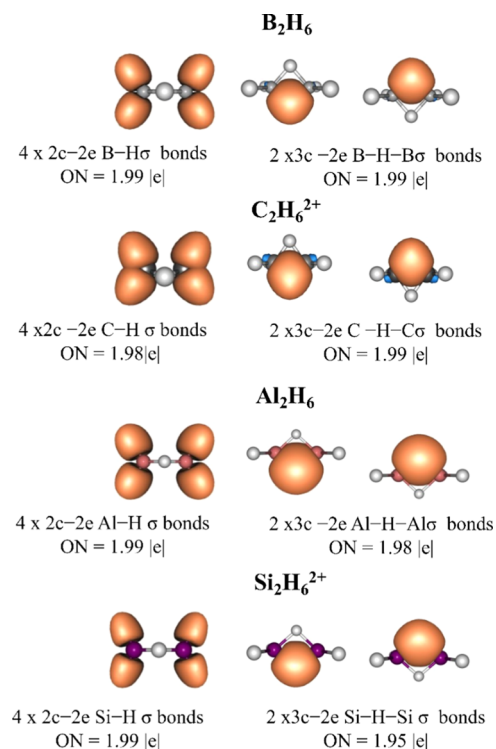
**Inverse Transmutation from Group XIV (C Group) to Group XIII (B Group).** The way in which the atoms of groups XIV and XIII are bonded is very different. In the case of group XIV (the carbon group), they can form classical bonds such as single, double, triple, and aromatic, in accordance with the octet rule. On the other hand, the electron deficiency of group XIII (boron group) leads to the formation of bonds that comply with the sextet rule or delocalized 3c–2e bonds. Two of the most famous compounds within group XIII are boranes and alanes, the simplest of each group being BH<sub>3</sub> and AlH<sub>3</sub>; these form localized 2c–2e bonds as can be seen in Figure 2a,c. When the methyl (CH<sub>3</sub><sup>•</sup>) and silyl (SiH<sub>3</sub><sup>•</sup>) radicals lose an electron, they convert into methenium (CH<sub>3</sub><sup>+</sup>) and silylium (SiH<sub>3</sub><sup>+</sup>) cations, respectively. Both cations are isoelectronic to BH<sub>3</sub> and AlH<sub>3</sub> and present similar geometry with a D<sub>3h</sub> symmetry. The bonding patterns of CH<sub>3</sub><sup>+</sup> (see Figure 2b) and SiH<sub>3</sub><sup>+</sup> (see Figure 2d) are identical, showing three localized 2c–2e bonds.



**Figure 2.** AdNDP bonding pattern for (a) BH<sub>3</sub>, (b) CH<sub>3</sub><sup>+</sup>, (c) AlH<sub>3</sub>, and (d) SiH<sub>3</sub><sup>+</sup>.

When CH<sub>3</sub><sup>+</sup> and SiH<sub>3</sub><sup>+</sup> dimerize, they form similar structures to diborane and aluminum hydride with a D<sub>2h</sub> symmetry, except for C<sub>2</sub>H<sub>6</sub><sup>2+</sup>, which suffers a slight deformation possessing a C<sub>2v</sub> symmetry. Olah et al.<sup>37</sup> studied the PES of C<sub>2</sub>H<sub>6</sub><sup>2+</sup>, suggesting that the borane-like structure is 12 kcal·mol<sup>−1</sup> above the global minimum, while for Si<sub>2</sub>H<sub>6</sub><sup>2+</sup>, the Al<sub>2</sub>H<sub>6</sub>-like structure is the most stable structure in its PES. The bonding pattern of these compounds are shown in Figure 3 and are similar to B<sub>2</sub>H<sub>6</sub> and Al<sub>2</sub>H<sub>6</sub> with four 2c–2e C–H and Si–H bonds and two delocalized 3c–2e bonds between C–H–C and Si–H–Si atoms.

Additionally, the bonding patterns for the aromatic B<sub>12</sub> and B<sub>11</sub>C<sup>+</sup> compounds have been analyzed. Jena and co-workers<sup>22</sup> attributed the anomalous stability of B<sub>12</sub> to a triple aromaticity:



**Figure 3.** AdNDP bonding pattern for B<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub><sup>2+</sup>, Al<sub>2</sub>H<sub>6</sub>, and Si<sub>2</sub>H<sub>6</sub><sup>2+</sup>.

peripheral and central  $\sigma$  aromaticity and  $\pi$  aromaticity. Yuan and Cheng<sup>38</sup> reported the AdNDP bonding pattern of  $B_{12}$  which is shown in Figure 4. It is possible to observe nine  $2c-2e$

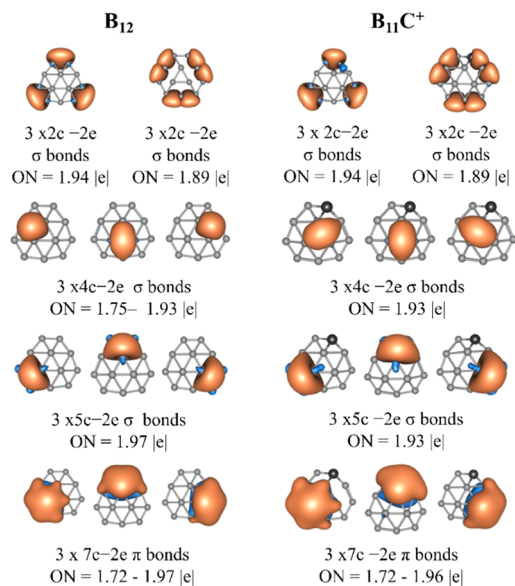


Figure 4. AdNDP bonding patterns for  $B_{12}$  and  $B_{11}C^+$ .

$2e$   $\sigma$  bonds located at the periphery of the ring, three delocalized  $4c-2e$   $\sigma$  bonds located in the central part of the cluster, three  $5c-2e$  bonds located in the outer  $B_9$  ring, and three  $7c-2e$   $\pi$  bonds, clearly showing a triple aromaticity character according to Hückel's rule.<sup>28</sup> An inspection of the isoelectronic compound  $B_{11}C^+$  shows an identical pattern to  $B_{12}$ , revealing that this compound has triple aromatic character, which could explain why this structure has been found as the global minimum by Islas et al.<sup>21</sup>

In the case of aromatic compounds such as  $Si_4^{2+}$ , we can see that the bonding pattern is identical to that of  $Al_4^{2-}$ .<sup>39</sup> Both have four lone pairs in each of the atoms of the ring. Additionally, they have three delocalized  $4c-2e$  bonds: one  $\pi$ , one  $\sigma$  radial, and one  $\sigma$  tangential. The results for  $Al_4^{2-}$  in Figure 5 are in agreement with the previous results that indicate that this compound is strongly  $\sigma$ -aromatic and weakly  $\pi$ -aromatic.<sup>40</sup> Nguyen and co-workers<sup>23</sup> found that the aromaticity in the  $Si_4^{2+}$  cluster is essentially  $\sigma$ -type. Our studies of quantification of the aromatic character by means of ring current strength indicate that both compounds have similar values and that 85% of aromaticity in both clusters is

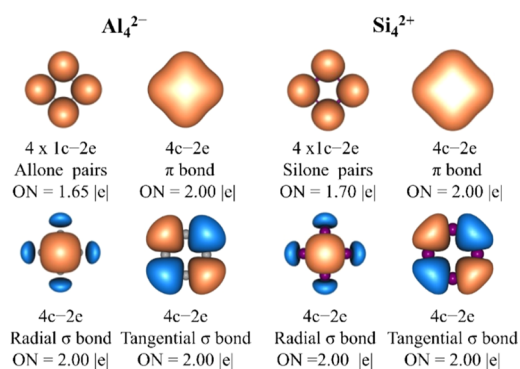


Figure 5. AdNDP bonding patterns for  $Al_4^{2-}$  and  $Si_4^{2+}$ .

due to  $\sigma$  contribution, while 15% is due to  $\pi$  contribution (see Table S1 in the Supporting Information). Results are in agreement with the results shown by Monaco et al.<sup>41</sup> for  $Al_4^{2-}$ . Moreover, results show that  $Si^+$  has been transmuted into  $Al$ , according to the following process:  $Al_4^{2-} \rightarrow ((Si^+)_4)^{2-} \rightarrow Si_4^{2+}$ , retaining the same geometry, bonding pattern, and for this case, a very similar aromatic character.

**Inverse Transmutation from Group XV (N Group) to Group XIV (C Group).** Group XV compounds, also called pnictogens, tend to form three bonds and together with the lone pair comply with the octet rule, as in the case of ammonia  $NH_3$ ; however, cationic compounds that possess pnictogen atoms tend to behave in a similar way to group XIV atoms. Two notable cases are those of the ammonium and hydrazinedium cations which present structures similar to methane and ethane, respectively (see Figure 6). In addition, the bonding of these cations presents an identical pattern to group XIV compounds.

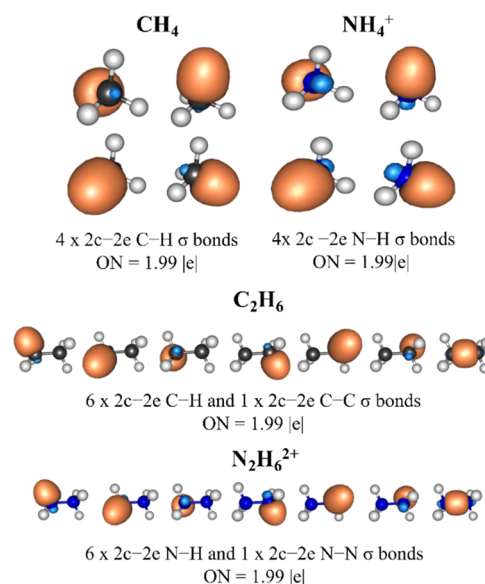
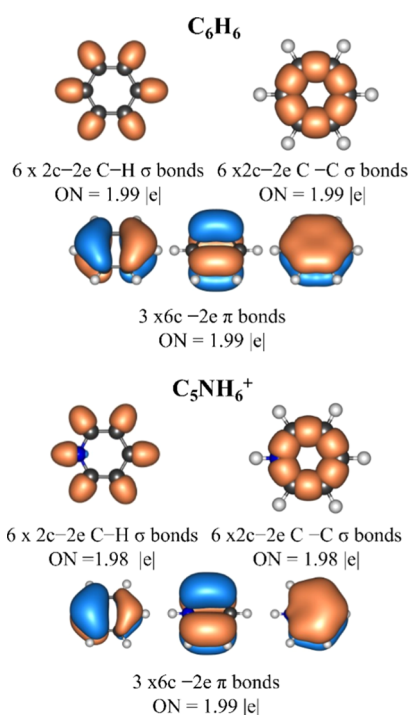


Figure 6. AdNDP bonding patterns for  $CH_4$ ,  $NH_4^+$ ,  $C_2H_6$ , and  $N_2H_6^{2+}$ .

Moreover, the aromatic pyridinium cation ( $C_5NH_6^+$ ) is isoelectronic and has an identical structure to benzene. Recently, we have reported that isoelectronic derivatives to benzene present a degree of similarity in aromaticity.<sup>42,43</sup> The bonding patterns for both compounds are presented in Figure 7, and it can be seen that these molecules present six localized  $2c-2e$  bonds corresponding to C-H and N-H bonds, six  $2c-2e$  bonds corresponding to C-C and C-N bonds, and finally, three delocalized  $6c-2e$  bonds in full agreement with Hückel's rule.<sup>44</sup> This leads us to believe that the cationic compounds of group XV have a behavior similar to those of group XIV, so we could state that they have been transmuted.

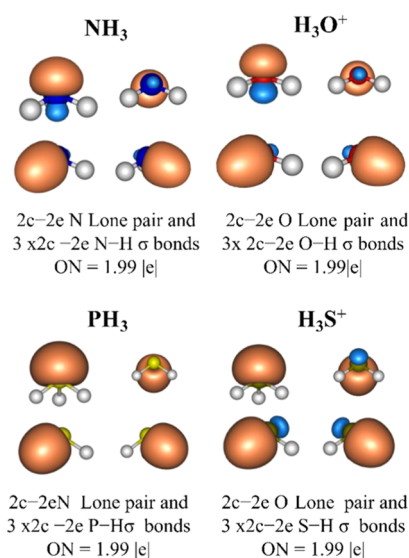
**Inverse Transmutation from Group XVI (O Group) to Group XV (N Group).** Chalcogens (XVI) can "transmute" into pnictogens (XV) by losing an electron. A couple of remarkable examples are hydronium ( $H_3O^+$ ) and sulfonium ( $H_3S^+$ ) cations which have structures and chemical bond patterns identical to those of  $NH_3$  and  $PH_3$ , respectively, with a lone pair in the chalcogen atom and three bonds located at





**Figure 7.** AdNDP bonding pattern for benzene and pyridinium cation.

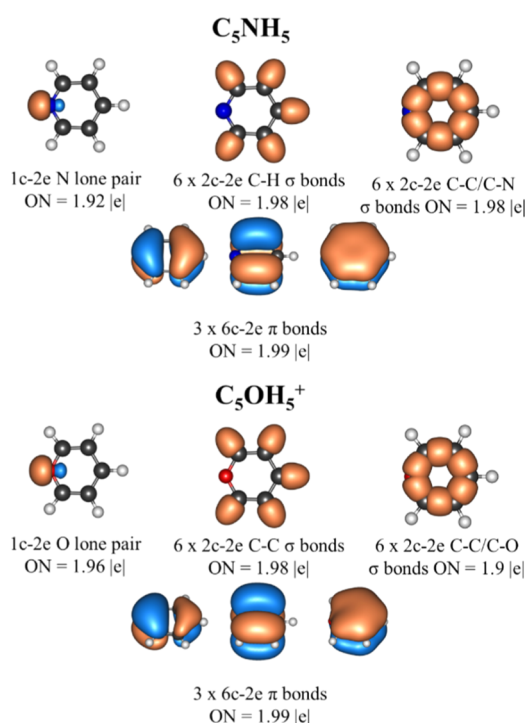
2c-2e in perfect agreement with the bonding pattern of the pnicogens (see Figure 8).



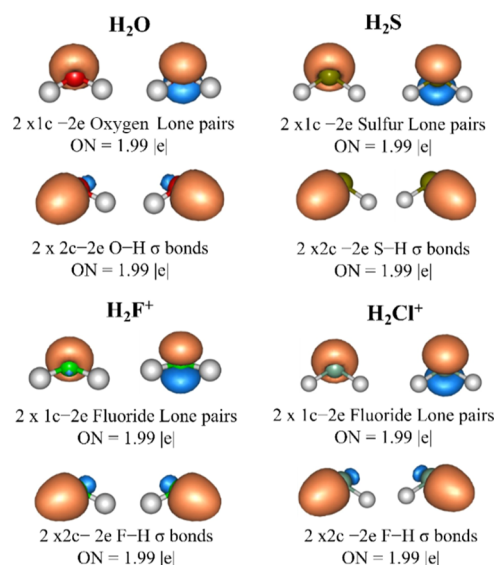
**Figure 8.** AdNDP bonding pattern for benzene and pyridinium cation.

As in the case of benzene and pyridinium, pyridine and pyrylium cations are isoelectronic and aromatic and present the same bonding pattern with a lone pair (1c-2e); five 2c-2e C-H bonds; six 2c-2e C-C, C-N, and C-O compounds; and finally, three delocalized 6c-2e complying with the Hückel's rule (Figure 9).

**Inverse Transmutation from Group XVII (F Group) to Group XVI (O Group).** Figure 10 shows the bonding patterns of simple compounds H<sub>2</sub>O and H<sub>2</sub>S, where the lone pairs s and p of the O and S atoms can be seen perfectly located with an



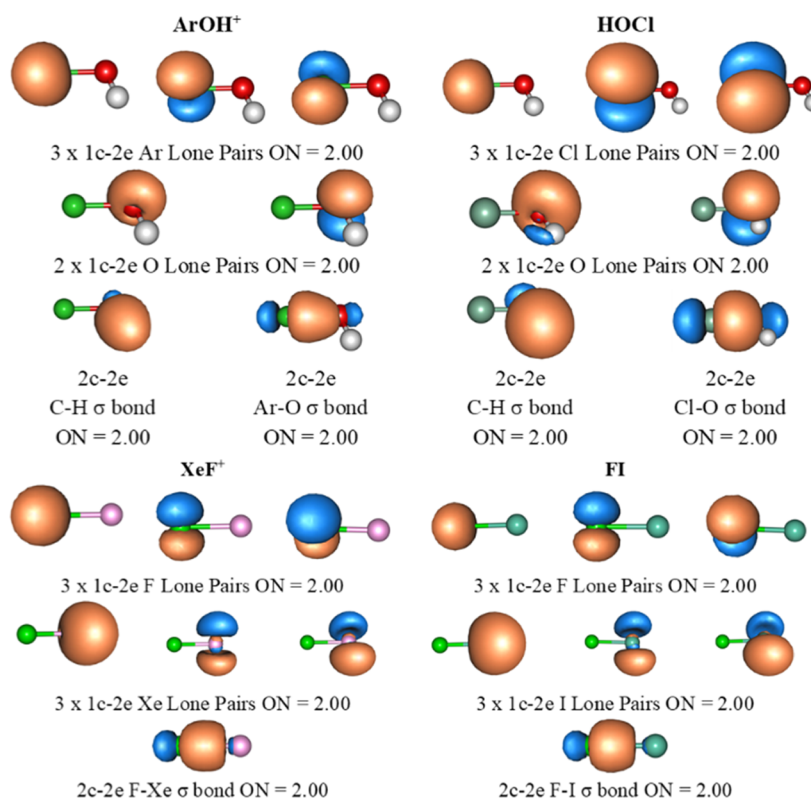
**Figure 9.** AdNDP bonding pattern for pyridine and pyrylium cation.



**Figure 10.** AdNDP bond patterns for H<sub>2</sub>O and H<sub>2</sub>S, and their inversely transmuted analogues H<sub>2</sub>F<sup>+</sup> and H<sub>2</sub>Cl<sup>+</sup>.

ON = 2.00|e|. Together with this, it is also possible to observe the located  $\sigma$  bonds O-H and S-H. It is also possible to see the bonding patterns of the transmuted compounds H<sub>2</sub>F<sup>+</sup> and H<sub>2</sub>Cl<sup>+</sup>, where the F and Cl atoms have exactly the same lone pairs, and the bonding pattern is similar. This leads us to consider that when a halogen loses an electron (X<sup>+</sup>), it acquires the behavior of a chalcogen atom.

**Inverse Transmutation from Group XVIII (He Group) to Group XVII (F Group).** The analysis of the bonding pattern for ArOH<sup>+</sup> and HOCl by means of AdNDP method can be seen at the top of Figure 11; both systems present three lone pairs in the form of 1c-2e bond for the Ar and Cl atoms. In the case of oxygen, the two lone pairs are also located at 1c-



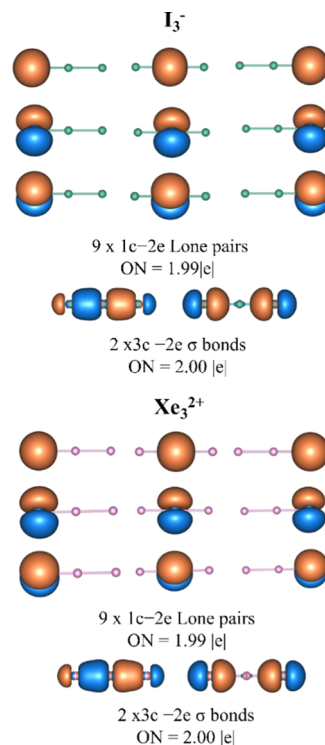
**Figure 11.** AdNDP bonding pattern for  $\text{ArOH}^+$ ,  $\text{HOCl}$ ,  $\text{XeF}^+$ , and  $\text{FI}$ .

2e. The  $\sigma$  bond corresponding to the O and H atoms is located with an occupancy of 2.00|e|. The most important detail is observed in the bond localized at 2c–2e corresponding to the  $\sigma$  bond between Ar–O and Cl–O, which present a similar pattern, except for the small polarization observed toward the oxygen in the  $\text{HOCl}$  molecule. For the case of  $\text{XeF}^+$  and  $\text{FI}$ , three lone pairs are presented at the top of Figure 9 for each atom; additionally, a 2c–2e  $\sigma$  bond is found. This is an indicator that this compound presents the behavior of an interhalogen compound.

The concept of inverse ET, like the original concept, can lead to the study of different compounds with exotic and interesting bond types, as is the case of the  $\text{Xe}_3^{2+}$ , which is an inversely transmuted form of the triiodide anion ( $\text{I}_3^-$ ), where each Xe atom has lost an electron. This compound has the same geometry and number of electrons as  $\text{I}_3^-$ , which has been studied by Pimentel,<sup>45</sup> proposing that this compound has a 3c–4e bond. The chemical bond of this hypervalent compound can also be seen as the average of two resonant structures.<sup>46</sup> The AdNDP bonding pattern in Figure 12 shows nine lone pairs, three in each iodine atom. Additionally, delocalized 3c–2e bonds complete the bonding pattern of this compound. In the case of  $\text{Xe}_3^{2+}$ , the bonding pattern is identical, and it can be said that this compound also presents a 3c–4e bond if we take into account Pimentel's point of view (see Figure S1).

## CONCLUSIONS

The present work shows that the ET concept can be extended to cases where an element with atomic number  $Z$  loses an electron, transmuted into a  $Z - 1$  element (inverse ET). Chemical bonding pattern studies according to the AdNDP analysis show that the systems containing main group elements



**Figure 12.** AdNDP bonding pattern for hypervalent  $\text{I}_3^-$  and  $\text{Xe}_3^{2+}$  compounds.

are analogous to simple known and well-characterized compounds. Therefore, when an atom from group  $X$  loses an electron, it inversely transmutes into an  $X - 1$  element. We hope that the inverse ET concept in conjunction with the original electron transmutation developed by Olson and

Boldyrev<sup>1</sup> can be explored in the future under different criteria, conformations, and combinations of elements to be used as the design criteria of novel, interesting compounds.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03865>.

Ring current strength values for Al<sub>4</sub><sup>2-</sup> and inversely transmuted Si<sub>4</sub><sup>2+</sup> at the PBE0-D3/def2-QZVP level, canonical orbitals proposed for Pimentel for explaining the 3c–4e bond, and cartesian coordinates (PDF)

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### Author Contributions

R.B.-G.: methodology, investigation, formal analysis; O.Y.: investigation, formal analysis; R.P.-R.: conceptualization, methodology, investigation, formal analysis.

### Notes

The authors declare no competing financial interest.

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