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Valence Shell Electron Pair Repulsion Theory Revisited: An Explanation for Core Polarization

Julen Munárriz,^{*[a,b]} Mónica Calatayud,^[b] Julia Contreras-García^{*[b]}

Abstract: Valence Shell Electron Pair Repulsion (VSEPR) theory constitutes one of the pillars of theoretical predictive chemistry. It was proposed even before the advent of the “spin” concept, and it is still a very useful tool in chemistry. This article proposes an extension of VSEPR theory to understand the core structure and predict core polarization in main group elements. We show from first principles (Electron Localization Function analysis) how the inner and outer core shells are organized. In particular, electrons in those regions are structured following the shape of the dual polyhedron of the valence shell (3rd period) or the equivalent one (4th and 5th periods). We interpret these results in terms of the “hard” and “soft” core character. All the studied systems follow this trend, providing a framework for predicting electron distribution in the core. We also show that lone pairs behave as “standard ligands” in terms of core polarization. The predictive character of the model was tested by proposing the core polarization of different systems not included in the original set (such as XeF₄ and Fe(CN)₆³⁻) and checking the hypothesis by means of *a posteriori* calculations. From the experimental point of view, the extension of VSEPR to the core region has consequences for timely crystallography. In particular, it enables to explain the core polarization proposed in the resolution of accurate X-ray structures. This result is illustrated for the particular case of α -silicon.

Introduction

The development of simple models that facilitate a reliable prediction and rationalization of molecular structures and properties is of great importance in current chemical research.^[1,2] In this regard, a good example of the predictive character of a simple energy model is the widespread Valence Shell Electron Pair Repulsion (VSEPR) theory. Specifically, it allows for predicting molecular geometries in terms of repulsions between electron pairs.^[3] This theory has proven to work well for main group-based systems,^[4] with only some exceptions, especially for complexes bearing a d⁰ central atom.^[5,6] Hence, it constitutes, in conjunction with other models, such as Lewis structures and electronegativity, a basic pillar of “*chemical intuition*” and structural analysis in chemistry.^[7,8]

When developing the concepts behind VSEPR, the repulsion between electron pairs is used to explain the organization of the valence ligands and lone pairs. However, as its name states, this theory is generally applied to the valence shell, and less attention has been paid to the core electrons.^[9,10] Herein we show that the principles that govern VSEPR theory can be applied to explain the spatial distribution of all the electrons – valence and core – in a given system. This generalization has obvious epistemological consequences, allowing to obtain a further understanding of the electronic structure of the core regions. Moreover, we also highlight its utility in the interpretation of new accurate crystallographic data.^[11]

Whereas VSEPR theory was postulated relying mainly on chemical intuition and the empirical observation of a great number of compositions and stoichiometries, we count nowadays with tools that are able to reveal electron localization from first principles. One of them is the Electron Localization Function (ELF).^[12] The ELF is related with the probability of finding electron pairs with opposite spins, which makes it an ideal tool for the identification of Lewis entities (the ELF maxima typically appear at bonds and lone pairs).^[13] It has demonstrated to be very useful in the understanding and prediction of chemical properties,^[14] as well as in the study of a wide variety of reactions, ranging from organic to biochemical and organometallic, among many others.^[15,16] Within the framework of this contribution, we should highlight the work performed by Gillespie *et al.*, who were able to explain the distortions from the VSEPR geometry on different metallic compounds by applying the ELF to study the interactions between the valence shell ligands and the outer core regions.^[9,17]

This type of analysis holds an inherent interest in the interpretation of new and more accurate spectroscopies. High energy^[18,19] and high pressure^[20] processes have led to interesting novel chemical phenomena where core electrons become bare or even leave the atom. This introduces the need to understand the subtle core electronic structure. As an example, the inclusion of core deformations in the resolution of X-ray data is a current field of development in crystallography.^[21]

Crystallographic structures are usually resolved by resorting to the multipolar approximation.^[22] In this approach, cores are kept frozen, whereas the valence deforms to fit the experimental structure factors by using multipoles.^[23] However, it was recently proposed that for the appropriate resolution of accurate data, the core regions should also be allowed to deform.^[11] Herein, we further confirm the existence of such deformations from a theoretical point of view, by reproducing and explaining the core deformations reported in α -silicon.^[24]

The paper is organized as follows. Firstly, we introduce the concept of the dual and equivalent polyhedron, which will allow us to set the geometrical basis of the model. Then, we analyze the maxima of the ELF in the core region of a set of

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VSEPR-geometry molecules with central elements belonging to the representative groups of the periodic table, so as to unravel the connection between the core organization and the valence shell distribution. In particular, we interpret the localization patterns that arise in a number of VSEPR molecular geometries, with central atoms belonging to the 3rd, 4th and 5th periods. Within those, we firstly focus on the core structure of molecular systems with stoichiometries AX₆, AX₄, AX₅ and AX₃ (in decreasing order of symmetry). Then, we evaluate the effect that valence shell distortions have on the core structure. The consistency of the results allows us to propose some inductive general rules that enable to predict core organization, which are summarized at the end of the paper. Finally, the predictive power of the model is checked by i) explaining the experimentally determined core polarization of α -silicon^[24] and ii) predicting the core polarization of some test systems which are outside the group we used for elaborating the model.

Results and Discussion

Historically, the organization of the outer core in metals has been studied by means of an analysis of the electron density maxima, within the Quantum Theory of Atoms in Molecules (QTAIM) approach.^[25] A principle known as Ligand Opposed Charge Concentration (LOCC) was put forward. It states that the core localization maxima are located in the opposite direction of the ligands so as to minimize the repulsion between electron pairs, as exemplified in Figure 1a for a tetrahedral and an octahedral geometry.^[26] Nonetheless, a mere opposition of electron pairs does not always explain the organization of the electron localization maxima predicted by the ELF. For example,

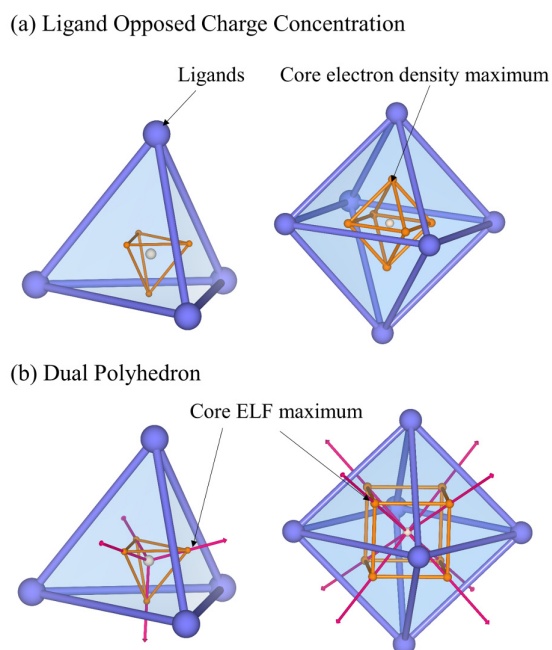


Figure 1. Schematic representation of a) the LOCC, and b) the dual polyhedron of a tetrahedron and an octahedron.

for a tetrahedral system such as SiF₄, the core ELF maxima have the shape of an inverted tetrahedron (in agreement with LOCC principle). However, for an octahedral system such as SF₆, the ELF localization maxima does not lead to LOCCs (which would result in an octahedron with the same orientation as the ligands, as depicted in Figure 1a). On the contrary, a cubic organization is observed. This leads to a reformulation of the principle guiding the outer core organization. Along this contribution, we show that in general, core organizations do not respond to an electronic localization opposed to ligands, but to a general organization in terms of the overall geometrical disposition of the ligands and the period to which the central atom belongs. This leads to the appearance of the dual and the equivalent polyhedra.

The dual polyhedron (DP) is the one that results from placing a vertex in the middle of the face of the original one (see Figure 1b). This principle allows to explain the shape of the localization maxima observed in the two previous examples, since the dual polyhedron of an octahedron is a cube (and *vice versa*); and that of a tetrahedron is another tetrahedron with an inverted orientation (see Figure 1b). These results anticipate the core structure being intimately related to the valence shell, and thus, the pertinent extension of VSEPR theory to the core regions. If this is the case, what happens as we go to the inner core? Whereas the previous seldom studies were carried out in the outer core,^[9] the concept of the dual polyhedron has pushed us to analyze the whole core structure of central atoms belonging to the 3rd, 4th and 5th periods. As previously stated, we have paid special attention to the relation between the ligand distribution in the valence shell and the core structure, and how distortions in the valence shell affect the core organization.

AX₆ stoichiometries. First, we considered simple octahedral molecules (O_h symmetry). The details of the calculations are presented in the Experimental Section. In particular, we began by AX₆⁽²⁾ geometries (A = S, P and Cl, in conjunction with X = H, F and Cl and the pertinent molecular charges, see Table S5). Notice that since the ELF respects the symmetry of the system, it only shows one maximum situated at the core position for the first core shell (2nd period elements). Hence, the ELF can only be used to analyze the outer core polarization of central atoms having at least two core shells, that is, which belong to the 3rd period onwards. In all the studied cases, the core region reflected the repulsion with respect to the valence shell, leading to the corresponding dual polyhedron: the localization maxima in the core for this set of molecules have the shape of a perfect cube (see Figure 2a for the case of PF₆⁻). In order to unravel whether this is a common trend for the outer core, the central atoms were substituted by those belonging to the 4th and 5th periods. Specifically, we considered Se, As, Br (4th row), Te, Sb and I (5th row). To our surprise, for these systems a different kind of core polarization was observed. Namely, the outer core directly polarizes following the valence shell, that is, the ELF maxima in the core are ligand oriented, having the shape of the equivalent polyhedron (EP). As a consequence, octahedra are observed for the first core shell in 4th and 5th row elements, as exemplified in Figures 2b and 2c for AsF₆⁻ and SbF₆⁻, respectively (see Table S5 for more examples). Since relativistic

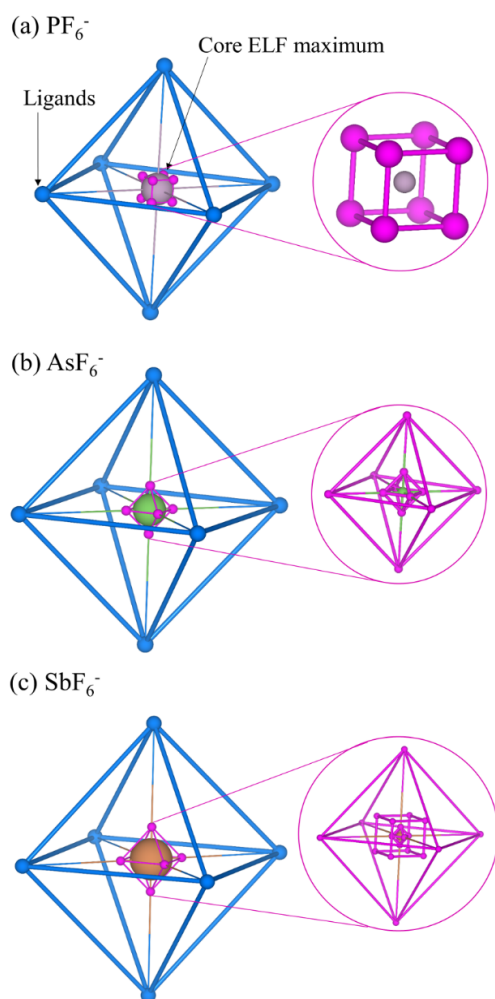


Figure 2. Outer and inner core polyhedra for a) PF_6^- , b) AsF_6^- and c) SbF_6^- . Fluoride ligands are depicted in blue, and core ELF maxima in purple.

effects may be important in these systems,^[27] we applied the relativistic zeroth order regular approximation (ZORA) in 5th row calculations, as explained in the Experimental Section.

We believe this finding paves the way to the extension of the chemical hard and soft character to the core regions.^[28] Atoms belonging to the 3rd period would exhibit a hard core character, and thus counter-polarize with respect to the electron pairs in the valence shell (DP). On the contrary, the outer core of atoms of the 4th row on would exhibit a soft core character. Hence, they undergo direct polarization (EP) with respect to the valence ligands. Notice that the inner core shells are also organized in terms of the dual and equivalent polyhedra (see the whole core structure depicted in Figure 2).

AX₄ stoichiometries. The previous results prompted us to extend the analysis to tetrahedral molecules (T_d symmetry). In particular, general stoichiometries $\text{AX}_4^{(2)}$ with central atoms belonging to the 3rd (A = Si, Al, P), 4th (A = Ge, Ga, As) and 5th (A = Sn, In, Sb) periods, in conjunction with X = H, F and Cl and the pertinent molecular charges were considered (see Table S6). Interestingly, the same general behavior as for AX_6 systems was observed. Namely, direct counter-polarization happened for 3rd row atoms. The dual polyhedron of the ligand shell was

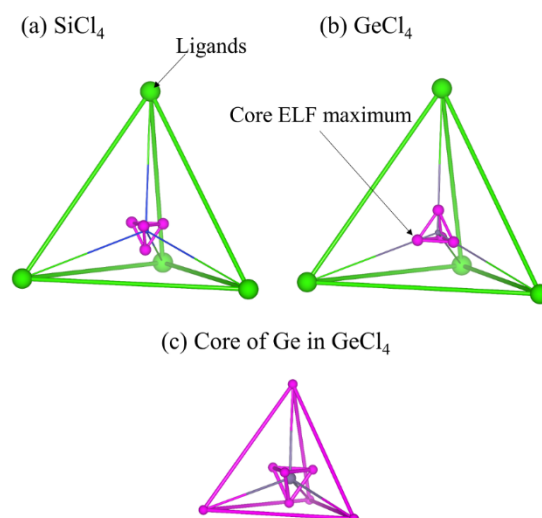


Figure 3. Outer and inner core polyhedra for a) SiCl_4 , b) GeCl_4 and c) Ge core of GeCl_4 . Chloride ligands are depicted in green and core ELF maxima in purple.

reproduced in the core, obtaining an inverted tetrahedron, as depicted in Figure 3a for SiCl_4 . On the contrary, 4th and 5th row atoms undergo direct polarization. As a consequence, the equivalent polyhedron was obtained in the core region; that is, a tetrahedron oriented in the same direction as the ligand shell (see Figure 3b for GeCl_4). Again, the same kind of behavior – organization in terms of the EP and the DP – is found in the inner core. As presented in Figure 3c for Ge (4th row), the outer core has the shape of the EP of the valence shell, while the inner core localization maxima form the DP of the outer core; see Figure S1 for additional details.

AX₅ stoichiometries. Less symmetrical valence shell geometries were also evaluated. In particular, we considered trigonal bi-pyramidal and triangular molecules, both with D_{3h} symmetry. For trigonal bi-pyramids, we analyzed $\text{AX}_5^{(2)}$ stoichiometries (A = Si, P and S for the 3rd row, A = Ge, As and Se for the 4th row, and A = Sn, Sb and Te for the 5th row; in conjunction with X = H, F, Cl and the proper charges, as shown in Table S7). Noteworthy, the ELF maxima in the outer core of 3rd row atoms have the shape of an inverted triangle (see Figure 4a for PH_5). That is, the core localization maxima adopts the shape of the DP of the equatorial triangle. As for the previous systems, this situation inverts when moving to 4th row atoms, which directly polarize with respect to the valence shell (see Figure 4b). Thus, the electron pairs in the outer core adopts the shape of a trigonal bi-pyramid (EP). Also in the agreement with the previous results, the inner core of 4th and 5th row atoms is structured in terms of the EP and DP, as shown in Figure S2.

AX₃ stoichiometries. The same principles were shown to hold for triangular molecules, $\text{AX}_3^{(2)}$ (A = Al, Si for the 3rd row, A = Ga, Ge for the 4th row and A = In, Sn for the 5th row, with X = H, F, Cl, and the appropriate charges; see Table S8). In molecular geometries with a central 3rd row atom, the outer core counter-polarizes, adopting the shape of a trigonal bi-pyramid with the central vertex opposed to the valence shell ligands (DP) and the two apical vertices perpendicular to the central

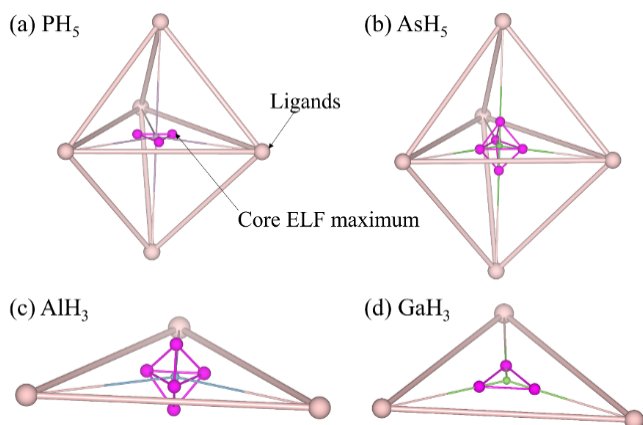


Figure 4. Outer core polyhedra for a) PH_5 , b) AsH_5 , c) AlH_3 and d) GaH_3 . Hydrogen atoms are depicted in light pink, and core ELF maxima in purple.

molecular plane (see Figure 4c). As depicted in Figure 4c, the expected DP polyhedron in AlH_3 (and in general AX_3 systems) appears. However, it is accompanied by another two axial localization regions. It should be noted that within the D_{3h} group, the axial and equatorial maxima form two different reducible representations. The appearance of these “extra” maxima on top of the predicted ones requires further analysis. As expected, the outer core from the 4th row on undergoes direct polarization (see Figure 4d). Thus, the electron localization maxima have the shape of a triangle oriented towards the ligands (EP). The inner core shells are also structured in terms of the DP and EP, as shown in Figure S3.

Geometry distortions. The possibility of inducing core deformations was also analyzed. First, we checked the effect of varying the central atom–ligand distances. Nonetheless, attempts to invert the core polarization by expanding and compressing the ligand shell did not lead to core structural changes. This result prompted us to analyze the effect of introducing symmetry variations. For that, we substituted one of the ligands in the valence shell by a different one. This procedure is represented in Figure 5a for the transformation of SiF_4 into HSiF_3 . As a consequence, the molecular geometry

evolves from tetrahedral (T_d symmetry) to trigonal pyramid (C_{3v} symmetry). The geometry of the localization maxima in the core was modified according to the variations in the valence shell. In particular, we obtained the DP of a trigonal pyramid (a distorted tetrahedron), which is another trigonal pyramid pointing in the opposite direction. Moreover, we evaluated this effect in 4th row atoms, by substituting Si by Ge. As expected, the outer core underwent direct polarization, and the electron localization maxima had the same geometry as the valence shell, *i.e.* a trigonal pyramid, see Figure 5a. It is worth noticing that this effect is transferred to the inner core, whose localization maxima have the geometry of the DP of the outer core: another trigonal pyramid. This way, we show that the modifications and distortions in the valence shell significantly affect all the core regions.

Another way to induce core modifications by means of geometry distortions without changing the VSEPR group is substituting a ligand by a lone pair (and introducing two more electrons in the central atom). Figure 5b shows the evolution of SiF_4 to PF_3 . Notice that the lone pair has the same effect as the ligand variation. Namely, the original tetrahedron in the core of SiF_4 transforms into a trigonal pyramid as a consequence of the formal substitution of a fluoride ligand by a lone pair. The same effect is observed when taking into account 4th and 5th row atoms. For the particular case of the substitution of P by As, the outer core directly polarizes towards the valence ligands and the lone pair, forming the EP; that is, an elongated trigonal pyramid pointing in the same direction as the original one. Then, as for the previous approach (fluorine substitution by hydrogen), the lone pair effect in the outer core also influences the inner core, where a complementary elongated trigonal pyramid appears. Since the lone pair lacks a core, this shows that the effects hereby observed are directly related to electron–electron interactions, and not to a crystal field effect given by the external potential (*i.e.* by the cores of the ligands).

α -silicon. Pushed by the previous results, we tested the ability of the model proposed herein to explain the core polarization experimentally determined in α -silicon.^[24] The extension of the multipolar approximation to the core has shown that the Si outer

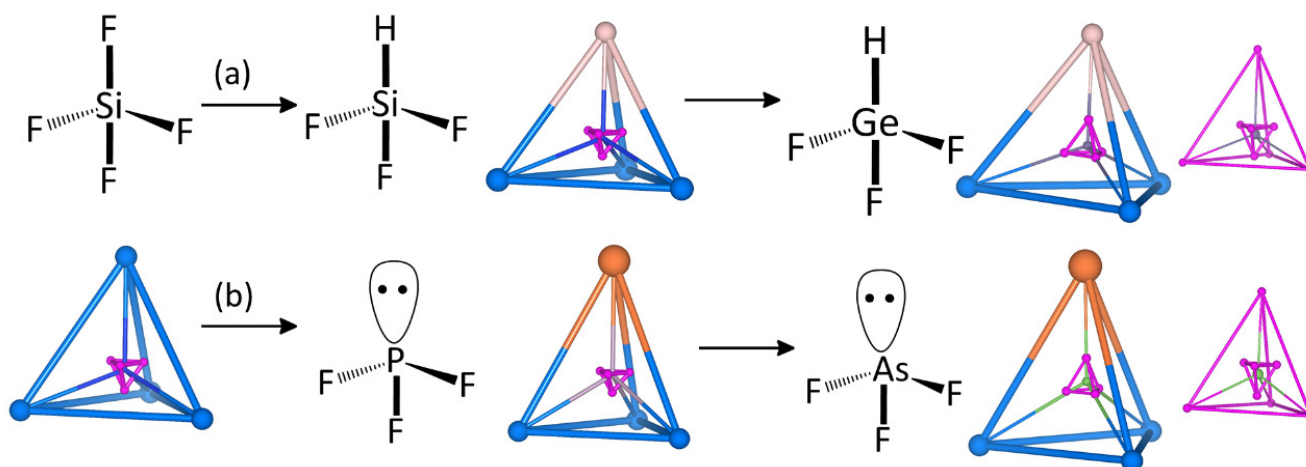


Figure 5. Evolution of the localization maxima in the core for the transformation of SiF_4 into a) HSiF_3 and GeHF_3 , b) PF_3 and AsF_3 . Fluoride ligands are depicted in blue, lone pairs in orange and core maxima in purple.

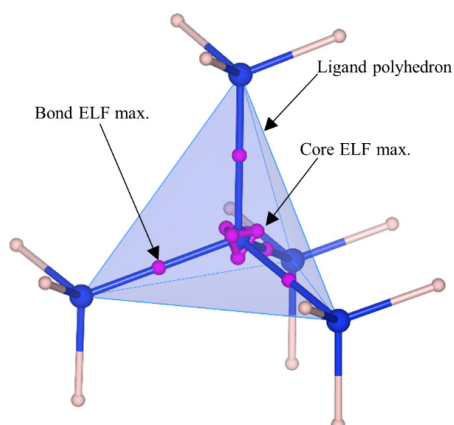


Figure 6. Model for α -silicon. The second coordination sphere has been replaced by hydrogen atoms. Si in blue, hydrogen in beige and ELF maxima in pink.

core is polarized in the shape of a tetrahedron, which is in an inverted position with respect to the tetrahedron formed by the first coordination sphere. This result is in agreement with our model, according to which the Si atom undergoes counter-polarization with respect to the bonded ligands (as previously shown for SiX_4 geometries, Figure 3a). This way, the Si core polarization has the shape of the DP of the valence ligands, that is, an inverted tetrahedron. In order to further confirm this result, we considered the model system reported in the original paper, $\text{Si}(\text{SiH}_3)_4$, and analyzed the ELF maxima in the Si core region.^[24] Notice that the expected behavior (an inverted tetrahedron in the Si core) was observed, as depicted in Figure 6. The agreement between the experimental results and the theoretical calculations further supports the validity of the theory.

The model. At this point, it may be convenient to summarize the general trends that can be derived from the previous results. We have found that, for the studied systems, all the central elements (which belong to the same periodic table row) behave equally in terms of core polarization, independently of the ligands that constitute the valence shell. More specifically, in all cases, the outer core of atoms belonging to the 3rd period undergoes counter-polarization, and the core localization maxima exhibit the structure of the dual polyhedron of the ligand shell. We interpret this behavior to be a consequence of the system tendency to minimize repulsive interactions between electrons in the valence and the outer core shell. Notice that according to our results, the core electrons do not necessarily form electron pairs. As such, we can observe, for example, a cube as a localization pattern for the outer core of the 3rd period elements, which does not lead to 2 electrons per vertex.

For the 4th and 5th periods, the outer core structure directly polarizes in the direction of the valence shell polyhedron. Thus, the localization maxima in the core have the shape of the direct polyhedron of the ligand shell. This highlights the softer nature of the core in 4th and 5th row atoms. This concept of “hard” and “soft” cores is in agreement with the relationship expected

between volume, compressibility and conceptual DFT hardness.^[29] Bigger atoms are expected to be easier to deform and polarize,^[30] also leading to less compressible materials.^[31,32] The coherence of the results support the predictive character of the polarization model we propose. Hence, it should be possible to predict the core structure of representative elements just by taking into account the position in the periodic table and the coordination number.

In this regard, we tested the predictive ability of the model by applying it to the structure of three different systems, which are not related with those considered for developing the previous discussion. In particular, we selected XeF_4 and $[\text{Fe}(\text{CN})_6]^{3-}$, whose core structures are shown in Figure 7a and 7b (see Table S11 for the cartesian coordinates).[†] The choice of XeF_4 lies on the fact that it has two lone pairs. Thus, it allows to test whether we can extend the results obtained for one-lone-pair systems to those with more lone pairs. Since Xe belongs to the 5th period, we would expect direct polarization of the outer core. The molecular geometry has the shape of a perfect square plus two lone pairs, which together form a compressed octahedron, as depicted in Figure 7a. Then, according to the previous results, the expected geometry for the outer core is a slightly compressed octahedron, which is the one that was found when performing the calculation (see Figure 7a). After that, we attempted to predict the core structure of a system bearing a transition metal. For that, we selected $[\text{Fe}(\text{CN})_6]^{3-}$, as a well-known example of a metallic complex where VSEPR theory holds.^[33] Since Fe belongs to the first transition metal row, we expect counter-polarization in the outer core. Thus, taking into account that the molecular geometry is octahedral, we expect that the localization maxima in the outer core have the shape of the DP of that octahedron, that is, a cube. This hypothesis was checked by performing the calculation, and, effectively, a cube shape was revealed for Fe outer core, as shown in Figure 7b. It is important to notice that the main analysis performed in this work was done with main group elements. Hence, we are cautious with the extension of these trends to systems bearing transition metals, and more systems should be studied to establish general and consistent trends.

Finally, we checked our ability to predict the core polarization in a crystal structure, as a test for crystallographic core polarization studies. We selected stishovite, a high pressure polymorph of silica.^[34] This system has a tetragonal $P4_2/mnm$ symmetry, in which Si is in an elongated octahedral coordination environment. Then, as Si belongs to the 3rd period, it should counter-polarize with respect to the valence shell and the core localization maxima should have the shape of an elongated cube (the DP of an elongated octahedron). In order to test this prediction, we constructed a cluster model, similar to the one considered for the analysis of α -silicon (see Figure S7 and Table S11). Our prediction is in agreement with the calculation (see Figure 7c).

[†] Notice that the study of these kind of systems was proposed by one of the reviewers after the initial model development.

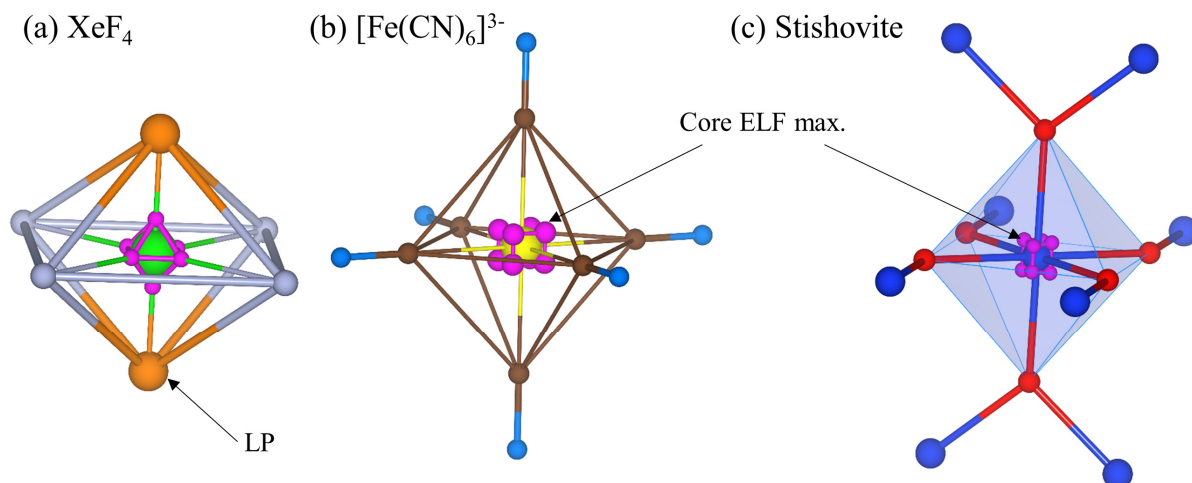


Figure 7. Outer core polyhedra for a) XeF_4 , b) $[\text{Fe}(\text{CN})_6]^{3-}$ and c) the model system for stishovite (the complete structure for this model is presented in Figure S4). Core ELF maxima are depicted in purple and lone pairs in orange.

Conclusions

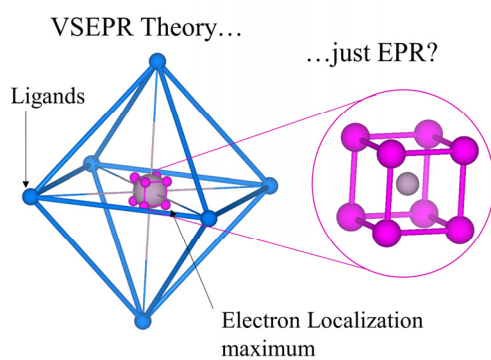
In conclusion, we have shown that the same physical principles that led to the development of VSEPR theory, that is, the molecular geometries adapting to minimize repulsion between electron pairs, can be used for predicting the core structure. Moreover, we have applied this model to understand in more detail the electrons organization in atoms with several core shells. Two different behavior patterns have been identified. On the one hand, for nuclei belonging to the 3rd period, the electron localization maxima in the core orient toward the center of the polyhedral faces defined by the valence ligands, so as to minimize electron repulsions. On the contrary, for 4th and 5th periods, several core shells appear, and the outer one orient toward the ligands, undergoing direct polarization. This observation suggests a pertinent extension of the chemical concepts of hardness and softness to the core region: 3rd row atoms would be harder than those belonging to the 4th and 5th periods. As a consequence, the spatial disposition of the outer core electrons of elements belonging to the 3rd period is that that minimizes electron repulsions with the valence. On the contrary, the outer core of atoms in the 4th and 5th rows undergoes direct polarization toward the valence shell. Besides, we have demonstrated that there is an intimate relation between the ligand shell and the core, as valence distortions are transferred to all the inner core shells. Finally, we have shown that the lone pairs behave as “*standard*” ligands in terms of core organization. The principle hereby described not only confirms the existence of core polarization, but also explains the experimentally found core spatial distributions in α -silicon. Hence, these basic principles can be used to help understand and predict core polarization in X-ray accurate data.

Experimental Section

Geometry optimizations and wavefunction calculations for ELF analyses were obtained through DFT calculations, by means of the Gaussian 09 program package.^[35] The CAM-B3LYP exchange-correlation functional was applied,^[36] in conjunction with the DGDZVP basis set, so as to be able to explicitly reproduce the electronic structure of the inner core of all the considered elements (up to the 5th period).^[37] The validity of the previous methodology was checked by using other functionals: B3LYP,^[38] PBE^[39] and PBE0,^[40] in combination with bigger basis sets: 6-311G(*d,p*),^[41] cc-pVTZ^[42] and def2-TZVP.^[43] We also applied Hartree-Fock (HF) to analyze whether the absence of electron correlation has a significant effect on the results. As explained in the Supporting Information (Tables S1–S4), the results obtained by varying the computational conditions led to consistent results. The calculation of the ELF and the analysis of its critical points were performed with the PROMOLDEN code.^[44] Images were produced with VESTA.^[45]

As relativistic effects may have an influence on the core structure of atoms belonging to the 4th and 5th periods, relativistic calculations were performed on a set of molecules so as to confirm the validity of non-relativistic calculations. We considered the zeroth-order regular approximation (ZORA) as implemented in the Orca 4.0 suite.^[46] An all-electron ZORA-def2-TZVP basis set was used in all the calculations,^[43] in conjunction with auxiliary SARC/J basis.^[47] We considered representative molecules of all the geometries included in the main discussion, with central atoms belonging to 3rd, 4th and 5th rows. In particular, the following set of molecules was chosen: AX₃: AlF₃, GaF₃, InF₃; AX₄: SiCl₄, SiF₄, GeF₄, SnF₄; AX₅: PF₅, AsF₅, SbF₅; AX₆: SH₆, SeH₆, TeH₆. In all cases, the same results as for non-relativistic calculations were obtained for the whole core structure of the 3rd and 4th periods and the outer core of the 5th period. Specifically, the inner core of InF₃, SnF₄ and SbF₅ molecules presented inverted polyhedra as for non-relativistic calculations. As a result, in order to provide accurate and reliable results, molecules involving 5th row central atoms were calculated by using relativistic calculations.

In this paper, the extension of VSEPR Theory to predict the electronic distribution of the core region is explored. The results show that there is an intimate and predictable relation between the valence and the core shells, broadening the scope of VSEPR to the core regions. This way, we shed light into the factors governing core polarization, which are important in current crystallography research.



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