

HClO₄ BONDING CHARACTERISTICS AGAINST FORMAL CHARGE PREDICTION AND HYPERVALENCE CONCEPT. SHOULD THESE CONCEPTS BE TAUGHT?^a

CARACTERÍSTICAS DEL ENLACE EN LA MOLÉCULA HClO₄ FRENTE A LA PREDICCIÓN POR CARGA FORMAL Y EL CONCEPTO DE HIPERVALENCIA ¿SE DEBEN ENSEÑAR ESTOS CONCEPTOS?

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ABSTRACT: Chemical bonding is a central topic in general chemistry courses. Lewis (1916) published a fundamental paper where he proposed a model based on localized electron pairs and, as a consequence, gave rise to the octet rule. However, the discovery of xenon fluorides and compounds such as SF₆ gave rise to the concept of “hypervalence” involving *d* orbitals in hybridization schemes. Currently, it has been demonstrated that *d* orbitals have a negligible participation in the bonds of such molecules and, in some cases, the octet rule is not violated. This article proposes a discussion about the concepts used in introductory chemistry lectures. Some models are useful and valuable from a pedagogical point of view, nevertheless, others are unnecessary and far from reality causing misconceptions and lack of interest since it is hard to rationalize inconsistencies found. The molecule of HClO₄ was selected to demonstrate that hypervalence concept, molecular structure selection based on formal charge rules and participation of *d* orbitals on bonds are not appropriate approximations. Bond orders and atomic charges determined through Natural Bond Orbital calculations indicate bonds between Cl and O atoms are mainly simple with a high ionic character.

KEYWORDS: Contents update; formal charge; hybridization; hypervalence concept; Lewis structure.

RESUMEN: El enlace químico es un tema central en cursos de química general. Lewis (1916) publicó un trabajo fundamental donde plantea un modelo a partir de pares de electrones localizados y da origen a la regla del octeto. Sin embargo, el descubrimiento de fluoruros de xenón y compuestos como SF₆ dieron lugar al concepto “hipervalencia” involucrando orbitales *d* en la hibridación. Actualmente, se ha demostrado que los orbitales *d* tienen una participación muy baja en los enlaces de dichas moléculas y en algunos casos, no exceden la regla del octeto. Este artículo plantea una discusión sobre los conceptos que se usan en cursos de química general. Algunos modelos son útiles y valiosos desde un punto de vista pedagógico, otros son alejados de la realidad generando conceptos erróneos y falta de interés por parte de los estudiantes, ya que es difícil racionalizar las inconsistencias encontradas. La molécula HClO₄ se seleccionó para demostrar que el concepto de hipervalencia, la selección de la estructura molecular basada en reglas de carga formal y la participación de orbitales *d* en los enlaces no son aproximaciones adecuadas. Los órdenes de

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enlace y cargas atómicas determinadas a través de cálculos “Natural Bond Orbital” indican que los enlaces Cl-O son principalmente sencillos con un alto carácter iónico.

PALABRAS CLAVE: Actualización de contenidos; carga formal; estructura de Lewis; hibridación; hipervalencia.

1. INTRODUCTION

Most general chemistry courses and textbooks incorporate the concept of Lewis structures as a fundamental component for understanding the behavior of matter by determining molecular structure, especially concerning p-block elements. Lewis (1916) proposed a series of steps to ascertain the number and type of bonds within a molecule. This method relies on observations and the knowledge of a big set of compounds, considering the count of valence electrons and, the hypothesis that two distinct atoms could give rise to the formation of a bond if each possessed at least one unpaired electron.

As a consequence, the pairing of electrons leads to bond formation. In the same paper, Lewis offered a wide discussion about polarity of bonds and, introduced what he termed the “rule of eight”, which later became known as the octet rule. He also proposed a cubical atom model to explain the formation of compounds through the repulsion of kernels and interaction of electrons located at outer shells of atoms involved (Lewis, 1916).

Continuing with the same model, Langmuir (1919) tried to apply the described concepts to the formation of additional compounds and attempted to reconcile these models with Bohr’s recent theory. Langmuir tried to identify common points by introducing several postulates discussing the symmetry and localization of electrons in cellular spaces distributed around the nucleus within the cubic model. Additionally, he coined the expression “octet rule” for the rule of eight initially proposed by Lewis.

Later on, Linus Pauling (1931) focused on the developments made by theoretical physicists to explain Lewis’ rules, proposing a new set of guidelines for electron-pair in bonds through the overlapping of eigenfunctions for the involved electrons. When the eigenfunction retains the identity, such as *p* orbitals on H-O-H (water), compounds should exhibit right angles between bonds. Therefore, hybridization schemes were necessary for explaining bond formation in compounds like CH₄, aligning with experimental measurements of 109.5° for angles in regular tetrahedron due to the change in the quantization of bond eigenfunctions.

Furthermore, Pauling developed trigonal quantization and the combination of *s*, *p*, and *d* eigenfunctions, resulting in planar squares or octahedral geometries for *sp*³*d*^{*n*} hybridization (Pauling, 1931). However, it was later suggested that these molecules could be more accurately described as electron-deficient compounds, offering a broader perspective and greater complexity to the bonding nature (Rundle, 1947).

The octahedral geometry, for example, could emerge from a *sp* hybrid orbital and, perpendicular to it, the

two remaining p orbitals positioned at right angles to each other. Each p orbital would be responsible for two bonds with only one electron pair, essentially forming a two electron-three center bond. The resonance among different equivalent positions would give rise to an octahedral bonding structure (Rundle, 1947).

Rundle explained in detailed that this approach aligns with the Pauli's exclusion principle, since just two electrons occupy the same orbital to form two different bonds. This indicates that "under appropriate conditions an atom may form more than one bond using a single orbital and using a single electron pair in that orbital" (Rundle, 1947).

This approach would allow to fulfill the octet rule which has been notably successful. Another strategy to avoid violating the octet rule involves the description of resonant structures including ionic interactions in molecules such as PCl_5 , where the polyatomic ion $[\text{PCl}_4]^+$ interacts with Cl^- , preventing to exceed the eight valence electrons (Durrant, 2015; Norman & Pringle, 2022; Noury *et al.*, 2002). In fact, a comparison between experimental and theoretical calculations for PF_5 revealed different charge distributions in equatorial and axial F atoms, suggesting a high ionic character in the axial position (Brown & Peel, 1968).

Despite various proposals and academic discussions, the concept of hypervalence was introduced by J. Musher (1969) following the discovery of xenon fluorides. This concept was coupled with the sp^3d^n hybridization. Hypervalent molecules refer to structures with more than four pairs of electrons around central atom, typically a nonmetal element from groups 15-18. Furthermore, central atoms that exceed the usual number of valences (octet rule) were described as electron donors (Musher, 1969).

Results obtained from nuclear quadrupole coupling studies on xenon fluorides and halogen fluorides led to the conclusion that central atom possesses an electronic density lower than expected for purely covalent bonds. Arguing that the bond should be partially ionic (Pitzer, 1963). For instance, in ICl_4^- , it was determined that Cl atoms carry negative charges, while I atom exhibits a positive charge with a very low participation of d orbitals (Pitzer, 1963). This observation could suggest a partial ionic bond rather than a sp^3d^2 hybridization. In addition, the energy required to promote an electron to $5d$ orbital in Xe compounds is large to consider d orbitals are involved in bonding (Kutzelnigg, 1984; Reed & Schleyer, 1990).

With the development and application of *ab initio* calculations to describe the bonding nature, it was convincingly demonstrated that participation of d orbital in "hypervalent" molecules is very low (Noury *et al.*, 2002). Electronic structure calculations for silicon, phosphorus, sulfur and chlorine fluorides were compared with experimental geometries and data from ^{19}F shift nuclear quadrupole resonance. Authors found no compelling reasons to include $3d$ -orbitals in bonding (Brown & Peel, 1968). Similarly, calculations that include spin-coupled descriptions indicated a similar conclusion, d orbitals should not be considered significant in these bonds (Cooper *et al.*, 1994).

SF₆ has been one of the most studied compounds (Cooper *et al.*, 1994; Gillespie & Robinson, 1995; Magnusson, 1990; Ponec & Gironés, 2002; Reed & Weinhold, 1986; Woon & Dunning, 2010). Reed & Weinhold (1986) determined through *ab initio* calculations the percentage of *d* orbital participation in SF₆ bonding, concluding the occupancy of 3*d*-orbitals is only one-sixth of what would be required for *sp*³*d*² hybridization. However, it has been suggested that *d* orbital participation is important (Bendazzoli *et al.*, 1968) but maybe, for electron back transfer from F atoms due to the compound's high ionic donor-acceptor character (Reed & Schleyer, 1990; Reed & Weinhold, 1986).

Computational results have clarified the significance of including *d* functions in some basis set employed for calculations of p-block elements. It is very similar to the effect of including *p* functions for a good representation of the H atom. It is important to note the use of term “function” instead of “orbital”. The inclusion of *d* functions is not primarily a chemical requirement but rather a mathematical necessity for improving polarization properties in geometry parameters and energy values (Cioslowski & Surján, 1992; Gillespie & Robinson, 1995; Magnusson, 1990).

Not only the participation of *d* orbitals was under discussion, but also the violation of the octet rule was questioned, *ab initio* calculations of “hypervalent” molecules with S as central atom led to the conclusion that S-O bond has a high ionic component and the bond order is close to one. In this way, octet rule might not necessarily exceed, as the valence electrons around central atom are fewer than is expected by covalent bonds according to classical Lewis theory (Cioslowski & Surján, 1992).

Similar results were determined for P-O bonds, indicating a substantial ionic character within these bonds, where O atoms seems to be surrounded by three lone pairs (Dobado *et al.*, 1998). Electron localization function was employed to calculate the total valence electrons around central atoms. In the case of SF₆, S is found to be surrounded by 7.68 electrons, suggesting the fulfillment of the octet rule (Noury *et al.*, 2002).

Furthermore, two very important conclusions were drawn. Firstly, the count of valence electrons around the central atom depends on electronegativity of the outer atoms. Secondly, there is not a specific characteristic or behavior capable to differentiate “hypervalent” molecules from those that obey the octet rule (Noury *et al.*, 2002). This was proposed before, through comparison between molecules of the second and third periods with similar reactivities, for example BF₃ - PF₅ and CF₄ - SF₆ leading to conclude that is pointless to classify them as “normal” or “hypervalent” molecules (Gillespie & Robinson, 1995).

The original definition of hypervalence was based on third-period elements since they have *d* orbitals available. However, molecules like neutral radical NH₄ and CLi₆ present anomalies under octet rule (Durrant, 2015). It was reported several years ago that even N or C can increase their valence using antibonding orbitals (Harcourt, 1968).

An important distinction exists between second-period elements and those from the third period onward. Second-period elements possess only an *s* inner orbital and, while their *s* and *p* valence orbitals are highly localized. Conversely, atoms in the third period and beyond have *s* and *p* core orbitals, with valence orbitals extending diffusively across a wider region of space (Kutzelnigg, 1984). This plays an important role in bonding, more than *d* orbital participation in higher atoms. It should be related with the size of atoms and the reduction of steric hindrance. A model involving electron-rich multicenter bond is closer to reality than *d* hybridization (Kutzelnigg, 1984).

Several hypotheses, such as recoupled pair bonding (Woon & Dunning, 2009; Woon & Dunning, 2010) or, in some cases hypercoordination (Ponec & Gironés, 2002) have been proposed for compounds that seem to exceed the octet rule based on Lewis structures. However, it is important to highlight that a drawing composed of symbols and lines is not a representation of a real chemical bond. Rather, it serves as a depiction for a specific stoichiometric formula that provides valuable information. Yet, a more detailed understanding is needed to precisely determine the nature of bonding in these compounds.

An attempt has been made to summarize the development of models used to explain chemical bonding in general chemistry courses, but another approach that seems to generate additional confusion was encountered: the formal charge. The initial idea of this paper was to establish a relationship between the formal charge in central atom and acid character in the series HClO_x , $x = 1 - 4$. However, upon initiating the analysis of computational results and exploring hypervalence dilemma; it was realized that a serious contradiction existed between the obtained geometry and the one favored by formal charge scheme.

The formal charge serves as a tool for determining the most suitable Lewis structure for a molecule when multiple resonant structures are possible. It is calculated by finding the difference between the valence electrons in an isolated atom and the number of assigned electrons in the Lewis structure (Chan & Goldby, 2020). It is important to mention that electrons assignment assumes equal electronegativity for both atoms, meaning that the electron pair is equally distributed between the atoms in the bond (Brown *et al.*, 2014; Parkin, 2006).

In order to select the most suitable Lewis structure, formal charges should be minimized in each atom. In case of remaining charges, the negative charge typically localizes at the most electronegative element (Brown *et al.*, 2014; See, 2009).

However, this approach encounters various known exceptions. For example, CO has a triple bond with the positive charge localized on O atom (Durrant, 2015). In the case of O_3 , there is a possibility of forming a cycle with all formal charges equal to zero, that is frequently the structure suggested by students unaware of the strain present in a three-membered ring. SO_4^{2-} molecular structure predicted is different to the experimental results discussed earlier. Consequently, this discrepancy in what is taught and what is observed may lead to confusion for first-semester students regarding the applicability of the rule. Such confusion often translates

into a lack of interest, misconceptions, and difficulties to understand chemistry and its fundamental concepts.

Different textbooks employed for introductory chemistry courses (Brown *et al.*, 2014; Chan & Goldby, 2020) introduce the concept of hypervalence and the determination of formal charges is promoted as a useful tool for selecting the most suitable Lewis dot structure. Chang's textbook includes tables with hybridization schemes involving *d* orbitals and indicates that an expanded octet is a frequent exception to the octet rule. It defines hypervalence as a function of existence of *d* orbitals capable of forming chemical bonds. Additionally, it describes the S atom in SF₆ molecule as using two of its five *d* orbitals, resulting in *sp*³*d*² hybridization (Chan & Goldby, 2020), (Brown's book does not mention *sp*³*d*^{*n*} hybridization (Brown *et al.*, 2014)).

Currently, in today's technologically advanced era, students are familiar with several technologies, utilizing electronic devices and having access to vast amounts of data. It becomes important to use more relevant approaches that enable a precise interpretation of the information they can find. ¿Why should students be taught with outdated paper models that frequently lead to inaccurate predictions? It is necessary to update contents of general chemistry courses, with more appropriate models and include examples that utilize available computational resources to enhance the understanding of matter behavior. This approach should surpass the reliance on antiquated concepts for predicting geometrical parameters that lead to misleading arguments (Norman & Pringle, 2022).

The objective of this paper is to encourage colleagues to engage in discussion concerning these approaches and ultimately facilitate the reaching of a consensus on a model that better approximates reality allowing to achieve the learning objectives of chemistry students.

With this in mind, I will describe HClO₄ molecule using classical models and electronic structure calculations to illustrate a detailed example of the aforementioned inconsistencies. Subsequently, it should be feasible to develop a syllabus proposing an alternative and modern approach for teaching molecular structure and derived properties.

2. COMPUTATIONAL METHOD

Gaussian 16 (Frisch *et al.*, 2019) were employed for optimization and Natural Bond Orbital (NBO) analyses for HClO₄ and ClO₄⁻. 6-31++G(3d,p) basis set in combination with B3LYP hybrid density functional theory was used. *p* function was included for representation of H atom and, given the importance of *d* function inclusion for stabilization of charge, 3*d* polarization functions were included for Cl and O atoms. NBO analysis were done as included in the *Gaussian 16* software for Wiberg bond index and charge distribution determination.

Charge distribution is important to determine electrostatic interaction (Martin & Zipse, 2005) and, consequently, the ionic character. Atomic charges were calculated through NBO as it is less sensitive to the employed basis set compared with Mulliken charges calculation (Reed & Schleyer, 1990; Reed & Weinhold, 1986).

This level of theory is computationally inexpensive and provides satisfactory results when compared to the experimental data. The goal is to enable both professors and students to replicate calculations and extract information on any computer.

3. RESULTS

The HClO_4 molecule has 32 valence electrons. Following Lewis theory, four possible structures can be proposed, as presented in Table 1 in descendent order of formal charges. Structure 1 obeys the octet rule but exhibits a notably high formal charge on central atom, with three of the O atoms carrying a negative charge. Considering formal charge minimization principle, this structure should be promptly dismissed. Consequently, structures 2 and 3 display a reduction in formal charge by redistributing lone pairs as double bonds. Finally, in Structure 4 all atoms hold a formal charge of zero by incorporating three double bonds.

Following the formal charge guidelines, Structure 4 would be selected as the most appropriate Lewis structure. In this scenario, HClO_4 would be categorized as a “hypervalent” molecule based on Musher’s definition (Musher, 1969). The Cl atom would exhibit a sp^3 hybridization employing d orbitals for double bonds, which is energetically unfavorable (Norman & Pringle, 2022).

Figure 1 shows optimized geometry for perchloric acid along with the atom numbering that will be used throughout the paper. The hydrogen atom is positioned staggered between atoms O_4 and O_5 , resulting in these atoms having equivalent bond distances and charges; while O_3 atom exhibits a slight difference, causing that ClO_3 group (with the removal of OH) to closely resemble the C_{3v} point group (Karelin, 1997). Reported dipole moment of HClO_4 is 2.17 D (Oh *et al.*, 2005), while the calculated value stands at 2.2 D, indicating a very good agreement with experimental properties, as can be seen in Table 2.

From Table 2 it is possible to conclude that, although the method employed in this paper is simpler than the reported computational strategies, results are in good agreement with both the experimental and theoretical values.

Table 3 shows Wiberg bond indices between bonded atoms in both HClO_4 and ClO_4^- . As can be seen, Wiberg bond index between Cl atom and O atoms non-bonded to H is closer to unity rather than two. This indicates the contribution of the structure with double bonds is considerably lower than expected according to the formal charge prediction. For further clarity, each C-H bond in CH_4 has a Wiberg bond index equal to

Table 1: Lewis dot structures for HClO₄, formal charge is shown when different to zero. Structures were drawn with (iChemLabs, 2023). Original creation

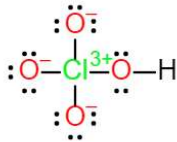
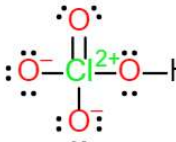
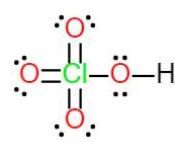
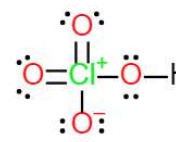
Numbering	Structure 1	Structure 2	Structure 3	Structure 4
Lewis dot structure				
Valence electrons around Cl atom	4 electron pairs around Cl atom / 8 valence electrons	5 electron pairs around Cl atom / 10 valence electrons	6 electron pairs around Cl atom / 12 valence electrons	7 electron pairs around Cl atom / 14 valence electrons

Figure 1: HClO₄ molecular structure and numbering. Left: front view, right: bottom view. Original creation.

0.95, Cl-Cl bond in Cl₂ molecule has an index of 1.01 and each C=O bond in CO₂ molecule has a value of 1.89. All these data were calculated at the same level of theory and basis set for comparison.

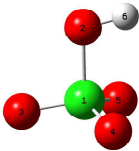
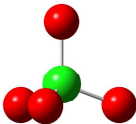
This implies that, although the formal charge approximation suggesting that Structure 1 was not a suitable representation for perchloric acid, it is the more contributing molecular structure compared to the structures with double bonds, even though they reduce formal charges, particularly Structure 4.

From the Wiberg bond indices, it can be calculated that Cl atom has a total of 4.62 bonds around. However, this does not necessarily imply that twice the valence electrons (9.2) are involved, as these bonds apparently have a high ionic character, as inferred from natural charge values. Specifically, the Cl atom exhibits a high positive charge (2.47), while O atoms carry negative charges exceeding 0.7. The O atom bonded to H displays the highest negative charge due to charge transfer from both Cl and H atoms.

Table 2: Geometric parameters for perchloric acid

Geometric parameter bond or angle	Experimental Casper et al., 1994	Computational CCSD(T) level Kalemos & Mavridis, 2009	Computational B97-1/aug-pc3+d method Boese & Martin, 2006	This work
Cl-O2	1.64 Å	1.64 Å	1.65 Å	1.68 Å
Cl-O3	1.41 Å	1.42 Å	1.42 Å	1.42 Å
Cl-O4	1.40 Å	1.41 Å	1.41 Å	1.43 Å
O2-H	0.98 Å	0.97 Å	0.97 Å	0.98 Å
Non-bonded distance O-O	2.38 Å		2.40 Å	
O3-Cl-O4	115.0 Å	115.1 Å	115.0 Å	115.2 Å
O4-Cl-O5	114.6 Å		113.8 Å	
O2-Cl-O3	101.5 Å	101.0 Å	100.9 Å	100.6 Å
O2-Cl-O4	104.2 Å		105.2 Å	104.9 Å
Cl-O2-H	105.0 Å	104.6 Å	105.7 Å	105.0 Å

Table 3: Wiberg bond index and NBO charge distribution. Original creation

Structure	Wiberg bond index	Natural charge
	Cl-O2 = 0.67 Cl-O3 = 1.33 Cl-O4 = 1.31 O2-H6 = 0.71	Cl = 2.47 O2 = -0.80 O3 = -0.72 O4 = -0.73 H = 0.52
	Cl-O = 1.17	Cl = 2.51 O = -0.88

If 9.2 valence electrons were considered, the classic Lewis theory would be referenced, wherein a pair of electrons is equally distributed between two atoms. Consequently, a hypervalent molecule would be discussed, meeting the original definition by Musher (1969). However, it is possible to calculate the percentage of ionic character of a bond by means of NBO program (Glendening *et al.*, 2018). In this case, it is around 32 %, indicating that Cl atom is not exceeding the octet as expected from literature review.

The ClO_4^- ion corresponds to T_d point group, consistent with a tetrahedral geometry. The Wiberg bond indices are highly similar to the average between the four Cl-O bonds in HClO_4 . In this way, the Cl atom exhibits a total Wiberg bond index of 4.68, remarkably close to 4.62 for the Cl atom in HClO_4 . This similarity could indicate the maximum capacity for electron donation by the Cl atom when bonded to oxygen.

Atomic charges can be estimated from geometry and dipolar moment measurements, or directly from electron densities obtained via X-ray crystallography. For example, S atom in K₂SO₄ has a positive charge of 4.3, without exceeding the octet rule (Durrant, 2015). Unfortunately, the experimental value for perchloric acid is not available.

Although Lewis model and octet rule have exceptions, they continue to be valuable tools for explaining molecular structures and bond formation (Norman & Pringle, 2022). However, it is necessary to emphasize the concept of a model. The same physical representation might be associated to different electronic interactions influenced by periodic properties such as atomic size and electronegativities of atoms. The importance of basing discussions on real data supported by these useful representations is to be highlighted. Special cases or exceptions should be explained carefully, avoiding direct reference to hypervalence or sp^3d^n hybridization.

4. CONCLUSIONS

Teaching the nature of chemical bond with the rigor of quantum mechanics in an introductory chemistry course is a challenging task due to its complexity. However, it is necessary to review the bonding models, ensuring their coherence both among employed models and with reality. Updating the course contents is necessary to facilitate a clearer comprehension of actual phenomena and chemical bonds.

The relevance of concepts such as hypervalence (including the sp^3d^n hybridization schemes) and formal charge should be reviewed. It is important to clarify that the formal charges are not compared with calculated natural charges nor experimental atomic charges. The aim was to show that formal charge approach is not appropriate for selection of a Lewis structure, as it often fails; the actual molecular structure does not correspond to the one with minimal formal charges.

Currently, an abundance of information exists regarding molecular properties, such as angles, bond lengths, dipole moments, and more. All of this information can be used to construct an extensive database, enabling discussions of real examples based on fundamental knowledge of bonding nature.

Today, as this paper is being written, I am considering potential inconsistencies within our teaching. For example, the electron count in a Lewis structure assumes that each bond is equally shared by the two atoms. And it is probable that polarity of bonds will be discussed in the same class, where a partial distribution of charges towards the most electronegative atom is explained. Even if students are not aware of these flaws, it will be more challenging for them to rationalize the concepts.

It is important to note that handling electronic structure calculations, selecting molecular and mathematical models, and interpreting results require a good understanding of theory, methods, and their limitations.

Continuous training and updating are essential for researchers and professors. For that reason, proposing discussions with the academic and scientific community for critical evaluation of models, their applications, and limitations is invaluable.

References

- Bendazzoli, G. L., Bernardi, F., Palmieri, P. & Zauli, C. (1968). The valence state of sulphur in sulphoxides: the role of 3d-orbitals. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 2186. <https://doi.org/10.1039/j19680002186>
- Boese, A. D. & Martin, J. M. L. (2006). Anharmonic force fields of perchloric acid, HClO₄, and perchloric anhydride, Cl₂O₇. An extreme case of inner polarization. *Journal of Molecular Structure*, 780–781, 310–316. <https://doi.org/10.1016/j.molstruc.2005.07.009>
- Brown, R., & Peel, J. (1968). VESCF-MO studies of molecules containing atoms from the second row of the Periodic Table. II. Properties of the fluorides of silicon, phosphorus, sulphur, and chlorine for a minimal basis set excluding 3d-orbitals. *Australian Journal of Chemistry*, 21(11), 2605. <https://doi.org/10.1071/CH9682605>
- Brown, T., Lemay Jr., E., Murphy, C., Bursten, B. & Woodward, P. (2014). *Química, la Ciencia Central* (12th ed.). Pearson Education.
- Casper, B., Mack, H.-G., Mueller, H. S. P., Willner, H. & Oberhammer, H. (1994). Molecular Structures of Perchloric Acid and Halogen Perchlorates ClOClO₃ and FOClO₃. *The Journal of Physical Chemistry*, 98(34), 8339–8342. <https://doi.org/10.1021/j100085a013>
- Chang, R. & Goldsby, K. (2020). *Química* (13th ed.). McGraw Hill Education.
- Cioslowski, J. & Surján, P. R. (1992). An observable-based interpretation of electronic wavefunctions: application to “hypervalent” molecules. *Journal of Molecular Structure: THEOCHEM*, 255, 9–33. [https://doi.org/10.1016/0166-1280\(92\)85003-4](https://doi.org/10.1016/0166-1280(92)85003-4)
- Cooper, D. L., Cunningham, T. P., Gerratt, J., Karadakov, P. B. & Raimondi, M. (1994). Chemical Bonding to Hypercoordinate Second-Row Atoms: d Orbital Participation versus Democracy. *Journal of the American Chemical Society*, 116(10), 4414–4426. <https://doi.org/10.1021/ja00089a033>
- Dobado, J. A., Martínez-García, H., Molina & Sundberg, M. R. (1998). Chemical Bonding in Hypervalent Molecules Revised. Application of the Atoms in Molecules Theory to Y₃ X and Y₃ XZ (Y = H or CH₃; X = N, P or As; Z = O or S) Compounds. *Journal of the American Chemical Society*, 120(33), 8461–8471. <https://doi.org/10.1021/ja980141p>
- Durrant, M. C. (2015). A quantitative definition of hypervalency. *Chemical Science*, 6(11), 6614–6623. <https://doi.org/10.1039/C5SC02076J>

- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G. & Barone, V. (2019). Gaussian 16, *Revision C.01*. Gaussian, Inc.
- Gillespie, R. J. & Robinson, E. A. (1995). Hypervalence and the Octet Rule. *Inorganic Chemistry*, 34(4), 978–979. <https://doi.org/10.1021/ic00108a032>
- Glendening, E. D., Badenhoop, J. K., Reed, A. E., Carpenter, J. E., Bohmann, J. A., Morales, C. M., Karafiloglou, P., Landis, C. R. & Weinhold, F. (2018). NBO 7.0.10. Theoretical Chemistry Institute, University of Wisconsin.
- Harcourt, R. D. (1968). Increased-valence theory of valence. *Journal of Chemical Education*, 45(12), 779. <https://doi.org/10.1021/ed045p779>
- iChemLabs. (2023, April 4). ChemDoodle. 2018.
- Kalemos, A. & Mavridis, A. (2009). Bonding Elucidation of the Three Common Acids H₂SO₄, HNO₃, and HClO₄. *The Journal of Physical Chemistry A*, 113(50), 13972–13975. <https://doi.org/10.1021/jp906294d>
- Karelin, A. I. (1997). Comment on “ Ab Initio Characterization of HOClO₃ and HO₄Cl: Implications for Atmospheric Chemistry”. *The Journal of Physical Chemistry A*, 101(13), 2518–2518. <https://doi.org/10.1021/jp960819s>
- Kutzelnigg, W. (1984). Chemical Bonding in Higher Main Group Elements. *Angewandte Chemie International Edition in English*, 23(4), 272–295. <https://doi.org/10.1002/anie.198402721>
- Langmuir, I. (1919). The arrangement of electrons in atoms and molecules. *Journal of the American Chemical Society*, 41(6), 868–934. <https://doi.org/10.1021/ja02227a002>
- Lewis, G. N. (1916). The atom and the molecule. *Journal of the American Chemical Society*, 38(4), 762–785. <https://doi.org/10.1021/ja02261a002>
- Magnusson, E. (1990). Hypercoordinate molecules of second-row elements: d functions or d orbitals? *Journal of the American Chemical Society*, 112(22), 7940–7951. <https://doi.org/10.1021/ja00178a014>
- Martin, F., & Zipse, H. (2005). Charge distribution in the water molecule-A comparison of methods. *Journal of Computational Chemistry*, 26(1), 97–105. <https://doi.org/10.1002/jcc.20157>
- Musher, J. I. (1969). The Chemistry of Hypervalent Molecules. *Angewandte Chemie International Edition in English*, 8(1), 54–68. <https://doi.org/10.1002/anie.196900541>
- Norman, N. C. & Pringle, P. G. (2022). Hypervalence: A Useful Concept or One That Should Be Gracefully Retired? *Chemistry*, 4(4), 1226–1249. <https://doi.org/10.3390/chemistry4040082>

- Noury, S., Silvi, B. & Gillespie, R. J. (2002). Chemical Bonding in Hypervalent Molecules: Is the Octet Rule Relevant? *Inorganic Chemistry*, 41(8), 2164–2172. <https://doi.org/10.1021/ic011003v>
- Oh, J. J., Drouin, B. J., & Cohen, E. A. (2005). The torsion–rotation spectrum of perchloric acid, HClO_4 . *Journal of Molecular Spectroscopy*, 234(1), 10–24. <https://doi.org/10.1016/j.jms.2005.07.012>
- Parkin, G. (2006). Valence, Oxidation Number, and Formal Charge: Three Related but Fundamentally Different Concepts. *Journal of Chemical Education*, 83(5), 791. <https://doi.org/10.1021/ed083p791>
- Pauling, Linus. (1931). The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules. *Journal of the American Chemical Society*, 53(4), 1367–1400. <https://doi.org/10.1021/ja01355a027>
- Pitzer, K. S. (1963). Bonding in Xenon Fluorides and Halogen Fluorides. *Science*, 139(3553), 414–415. <https://doi.org/10.1126/science.139.3553.414>
- Ponec, R. & Gironés, X. (2002). Chemical Structures from the Analysis of Domain-Averaged Fermi Holes. Hypervalence and the Nature of Bonding in Isocoordinated Molecules SF_6 and CLi_6 . *The Journal of Physical Chemistry A*, 106(41), 9506–9511. <https://doi.org/10.1021/jp026188l>
- Reed, A. E. & Schleyer, P. v. R. (1990). Chemical bonding in hypervalent molecules. The dominance of ionic bonding and negative hyperconjugation over d-orbital participation. *Journal of the American Chemical Society*, 112(4), 1434–1445. <https://doi.org/10.1021/ja00160a022>
- Reed, A. E. & Weinhold, Frank. (1986). On the role of d orbitals in sulfur hexafluoride. *Journal of the American Chemical Society*, 108(13), 3586–3593. <https://doi.org/10.1021/ja00273a006>
- Rundle, R. E. (1947). Electron Deficient Compounds 1. *Journal of the American Chemical Society*, 69(6), 1327–1331. <https://doi.org/10.1021/ja01198a028>
- See, R. F. (2009). Which Method of Assigning Bond Orders in Lewis Structures Best Reflects Experimental Data? An Analysis of the Octet Rule and Formal Charge Systems for Period 2 and 3 Nonmetallic Compounds. *Journal of Chemical Education*, 86(10), 1241. <https://doi.org/10.1021/ed086p1241>
- Woon, D. E., & Dunning, T. H. (2009). Theory of Hypervalency: Recoupled Pair Bonding in SF_n ($n = 1-6$). *The Journal of Physical Chemistry A*, 113(27), 7915–7926. <https://doi.org/10.1021/jp901949b>
- Woon, D. E. & Dunning, T. H. (2010). Recoupled Pair Bonding in PF_n ($n = 1-5$). *The Journal of Physical Chemistry A*, 114(33), 8845–8851. <https://doi.org/10.1021/jp102236a>