



“Hypervalency” and the chemical bond

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ABSTRACT

Bonding in chemistry refers to the stability of molecules, therefore it is of paramount importance to natural sciences and certainly to all aspects of life. Yet bonding is a chameleon-like fuzzy concept, leaving enough space to the sprouting of a variety of “theories” supposedly explaining the structure and bonding of molecular systems. Admittedly some of these “theoretical ideas” played a constructive and useful role to the development of chemistry in the last one hundred years, however they are no longer needed. Intertwined with binding the hypervalency definition introduced half a century ago, started to be used not only for communication purposes as intended, but as an “explanation” of the structure and bonding. In the present communication and within the spirit of nonproliferation of redundant concepts, we have tried to prove that bonding between atoms can be understood and clarified based solely on the tenets of quantum mechanics as applied to molecules. More specifically the undisputable role of the excited state of atoms in the bonding process is emphatically projected. Clearly chemistry is an excited state rather than a ground state field.

1. Introduction

The fundamental dogma-conjecture in Science is that the inner working mechanism of the Cosmos can be interpreted through a hierarchy of Physical Laws the origin of which is, clearly, beyond this report. The intertwining concepts of consistency and/or economy of these Laws are deeply rooted in the scientific community for reasons of necessity. The need for conceptual economy, tantamount to catholic clarity to all aspects of human activity has been expressed admirably by Ockham’s razor dictum some 700 years ago [1]: “multiplicity ought not to be posited without necessity.” Ockham’s razor still holds supreme nowadays particularly in the natural sciences.

Chemistry is a low energy, vast, and very complicated field. This complexity arises because a small (118 by now) and relatively “simple” number of entities called atoms can be combined in a myriad of ways to form, in principle, an infinite number of stable (bound) entities called molecules. The latter show astonishing properties as compared to their constituents, the atoms. A molecule M can be defined as a bound conglomerate of its constituents atoms; symbolically $M = \sum_{k=1}^N z_k A_k$ where Z_k is the atomic number of atom A_k and N the total number of atoms in M (Of course, this is not an equation in a mathematical sense, that is, $A = B$). The stability (boundedness) of a specific configuration of M is controlled by its total energy $E(M)$ as compared to the sum of the energies $E(z_k A_k)$ of the N atoms A_k . We can write $E(M) = \sum_{k=1}^N E(z_k A_k) - D$ where $D(> 0)$ is the total binding energy of M with respect to N noninteracting atoms. It is a fact that in general, D , in absolute numbers, is but a minute fraction of either E

(M) or $\sum_{k=1}^N E(z_k A_k)$. For a bound molecular system $E(M) < \sum_{k=1}^N E(z_k A_k)$ but, of course, $E(M) \approx \sum_{k=1}^N E(z_k A_k)$. With no doubt the vagaries, mysteries and a general vagueness or esotericism that surrounded and tortured chemistry for so many years were completely dissolved by the twentieth century advances in science along with the advent of quantum mechanics. Nobody seems to question seriously by now the famous aphorism by Dirac already expressed in 1929: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the *whole of chemistry* are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too *complicated* to be soluble.” [2] (emphasis added by the authors).

Despite the explosive progress and fearsome power of digital computers and computer codes during the last sixty years, the word *complicated* of Dirac’s aphorism is still with us. The accurate solution of the Schrödinger equation for even a relatively “small” molecule, say 2 to 4 or 5 nuclei and about 50 electrons and within the clamped nuclei approximation, is not a simple problem [3]. Interpreting the results of its approximate solutions, *i.e.*, wave functions (amplitudes), can even be harder. This abstruseness in determining the “personality” of a molecular system via the Schrödinger equation led over the years to the development and adoption by chemists of a variety of empirical and admittedly useful concepts, yet vague, conflicting and of dubious and circular nature. To mention a few: *resonance* [4], *hyperconjugation* [4], the *VSEPR* (valence shell electron pair repulsion) model, and numerous other concepts, mostly pertaining to energy stabilization and bonding. Within the Ockham’s razor dictum and focusing on the concept-definition of

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hypervalency, we will try to show that bonding in general can be understood in a simple, facile and straightforward manner, shaking off all kinds of extraneous and cyclically defined, thus confusing, concepts. The use of molecular orbitals (MO) and their classification as bonding, antibonding or nonbonding will also be avoided; simply it is not needed. Although MOs are of “technical” importance, they are not the best approach in the understanding of the chemical bond and its characteristics.

Some obvious but yet basic tenets in this endeavor follow: (a) molecules are composed of atoms, (b) atoms have an infinite number of excited states, (c) a *bona fide* two electron bond is described by the spin function $\Theta(1,2) = 1/\sqrt{2} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$, (d) the cause of the “hypervalent bonding” is an energy stabilization interplay between bond strengths and excited states of a “central” atom or “unit” of a molecule, and (e) quantitative results can only be obtained by accurately solving the Schrödinger equation.

2. Hypervalency

The term “hypervalent” was introduced in 1969 by J.I. Musher in order to describe and classify molecules that do not obey the “traditional” rules of valency [5]; see as well Refs. [6] and [7] and references therein. Musher wrote:

“We classify as “hypervalent” molecules and ions all these molecules and ions formed by elements in Groups V–VIII of the periodic table in any of their valences other than their lowest state chemical valence of 3, 2, 1, and 0, respectively. We refer to these molecules as hypervalent (or HV) since they involve atoms, called donor atoms, which exceed the number of valences allowed them by traditional theory, and thus utilize more electron-pairs of bonding than provide stability in the Lewis–Langmuir theory.”

With today’s notation Musher refers to columns 15–18 of the periodic table, while his “definition” reflects the feelings of the chemical community at that time. We also think that he never intended a definition to become an explanation to the question, for example, “what is the nature of bonding in N_2O ?”, the answer to be the “property of hypervalency”. A cyclic answer, obviously problematic and clearly alluding to exceptions to the traditional rules of normality.

In what follows we will try to show that hypervalent molecules are far from being exceptions, rather the contrary, while the definition of hypervalency perhaps useful half a century ago, it is not needed any more. We insist on the Ockham’s razor dictum or, to put it more generally, onto a “geometrization” of Science.

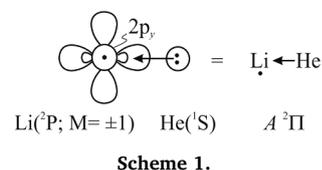
3. Results and discussion

In this account we shall present the electronic structure of certain molecules with unusual (“supervalent”) bonding character. Because excitation of atoms is central to our discussion, the molecules examined are presented in ascending atomic number of the atom excited in order to establish conducive bonding features.

Unless otherwise stated we employed the cc-pVTZ basis set [8] with single reference (CCSD(T)) and/or multireference (MRCI) computational approaches. The MOLPRO suite of programs [9] has been employed for all reported calculations.

3.1. Lithium (Li)

The electronic configuration of the ground state of the Li atom is $1s^2 2s^1$ (2S). In its ground state it can form a sigma (σ) bond with an H (2S) atom, *i.e.*, LiH ($X^1\Sigma^+$), but it is not expected to bind to a closed shell atom (or molecule) such as He (1S); yet it does. The first excited state of LiHe ($A^2\Pi$) not only exists but has an experimentally measured binding energy of $D_e = 1020 \pm 20 \text{ cm}^{-1}$ ($= 2.92 \pm 0.06 \text{ kcal/mol}$) at $r_e = 1.783 \pm 0.016 \text{ \AA}$ with respect to Li (2P) + He (1S) [10]. Recall that the Li ΔE ($^2P \leftarrow ^2S$) is 1.848 eV. A binding energy of $D_e = 2.92 \text{ kcal/mol}$ for such a system points to a chemically bound (non van der Waals)



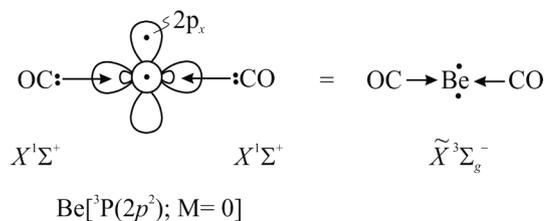
species that has been studied theoretically by Kerkines and Mavridis [11]. The two atoms are bound together through a harpoon like σ dative bond from He (1S) to Li (2P ; $M = \pm 1$). The valence–bond–Lewis (vbL) diagram (see Scheme 1) shows succinctly what is happening inside the molecule.

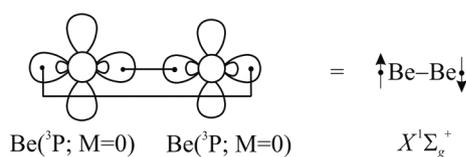
The best theoretical D_e value is $1011.2 \pm 2.8 \text{ cm}^{-1}$ ($= 2.891 \pm 0.008 \text{ kcal/mol}$) at $r_e = 1.790 \text{ \AA}$ obtained as a complete basis set limit based on a sequence of MRCI/aug-cc-pV (D, T, Q, 5) Z calculations. The proposed binding mechanism reveals another interesting possibility. A second He (1S) atom can also bind to LiHe ($A^2\Pi$) through the same mechanism giving rise to $LiHe_2$ (\tilde{A}^2B_1 , $\angle HeLiHe = 100.2^\circ$) with a $D_e(HeLi-He)$ value of 939.1 cm^{-1} very close to the $D_e(Li-He)$ ($= 1011.2 \pm 2.8 \text{ cm}^{-1}$). An identical mechanism is also found in LiRg ($A^2\Pi$) where Rg (rare gas) = Ne [12], and Ar or Kr. [13] The Li atom in its first excited 2P state provides room for the formation of a dative bond with the electron rich Rg systems; see Scheme 1 The same binding mode applies also to the less elementary cases of Li[CO] and Li[CS] [14]. Both CO and CS species can share an electron pair from either side thus creating σ dative bonds. The LiCO and LiCS $^2\Pi$ states are bound by 38 and 70 kcal/mol, respectively, with respect to Li (2P) + CO/CS ($X^1\Sigma^+$), while the LiOC and LiSC $^2\Pi$ states are also bound by about 8 and 40 kcal/mol, respectively. Notice, that LiCO ($^2\Pi$) lies about 4.5 kcal/mol above the “unbound ground state”, while LiCS ($\tilde{X}^2\Pi$) is the ground state.

3.2. Beryllium (Be)

The Be atom is a closed shell, $1s^2 2s^2$ (1S) atom, with its first excited 3P ($2s^1 2p^1$) state lying 2.73 eV higher. Its closed shell ground state suggests that Be could not form any chemically bound species, but surprisingly enough Be has a rich chemistry [15]. Under normal temperature and pressure conditions pure Be is a metal; it is reminded that its melting point is 1278°C . Its chemistry appears to defy the “traditional” Lewis–Langmuir theory (*vide infra*) and one can wonder where this valency comes from. It is obviously true that a significant attractive interaction between two tightly closed systems like Be (1S) and He (1S) would be an oddity. And this is indeed true but when the Be (1S) atom gets promoted to its doubly excited 3P ($2p^2$) state, 7.40 eV ($= 170.65 \text{ kcal/mol}$) higher, then the He atom penetrates unobstructed and that interaction features a stunning binding energy of $D_e(^3\Sigma^-) = 6251 \text{ cm}^{-1}$ ($= 17.87 \text{ kcal/mol}$) at the QCISD(T) level of theory [16]. The same mechanism applies to the $\tilde{X}^3\Sigma_g^-$ state of (OC:) \rightarrow Be \leftarrow (:CO) [17] (see Scheme 2) or in the \tilde{X}^1A_1 state of $Be(CO)_3$ [18] where a doubly excited Be (3P)/(1D) atom provides the necessary space for two/three:CO electron pairs to create two/three dative bonds, respectively.

Interestingly enough both systems are stabilized by $\approx 185 \text{ kcal/mol}$ with respect to Be (3P) + 2CO ($X^1\Sigma^+$) [17], or Be (1D) + 3CO ($X^1\Sigma^+$) [18], respectively. The most amazing thing a Be atom can experience

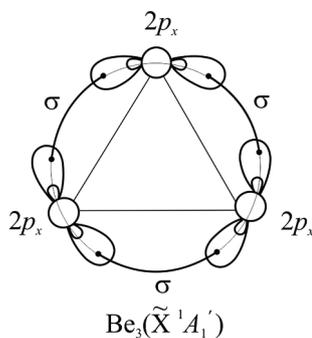




Scheme 3.

occurs when four NH₃ molecules approach it in a tetrahedral arrangement. The ground state of the complex consists of a Be(NH₃)₄²⁺ core with an electron pair in an *s* type diffuse orbital delocalized over the core's periphery [19]. The ³P (2s¹2p¹) Be state is also responsible for the binding in both the Be₂ (X¹Σ_g⁺) and Be₃ (\tilde{X}^1A_1') molecules with D_e = 2.30 (expt D_e = 2.67 kcal/mol) [20] and 25 kcal/mol with respect to three ground (¹S) Be states at the MRCl/aug-cc-pVQZ level, respectively [21]. Notice that the binding energies with respect to the excited state atoms are 128 and 214 kcal/mol for the diatomic and triatomic, respectively. There are two sigma bonds in Be₂ between two excited Be atoms (see Scheme 3), while in Be₃ each excited Be atom forms two single σ bonds with each of its neighbors (see Scheme 4).

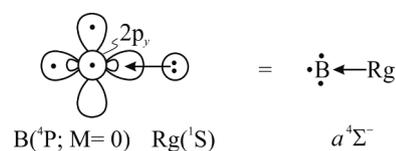
Based on the electronic structure of the neutral Be₂ dimer we can also understand the existence of Be₂⁻ in both of its two X²Π_u and 1²Σ_g⁺ states [21]. It would be otherwise impossible to combine a closed shell atom, Be (¹S), with a nonexistent Be⁻ anion. Be⁻ exists but with respect to the Be (³P) state that is being “trapped” inside the dimer [22]. It should be emphasized here that both molecules, Be₂ (X¹Σ_g⁺) and Be₃ (\tilde{X}^1A_1'), are stable closed shell species with the *in situ* Be atoms in their first excited ³P (2s¹2p¹) state. Needless to mention that Be₂ and Be₃ are hypervalent molecules. It is insightful to contrast cyclopropane (C₃H₆ = (CH₂)₃) to Be₃; in both species the constituent “units” Be (³P) and CH₂ (\tilde{X}^3B_1) have similar valence electronic distributions. The bonding vBL diagram of (CH₂)₃ is identical to that of Be₃ (Scheme 4) but with the two extra electrons of carbon “saturated” by the two H (²S) atoms; see also Ref. [23]. Of course cyclopropane is hypervalent as related to the ⁵S state of the carbon state (see below).



Scheme 4.

3.3. Boron (B)

The boron atom with a Hartree–Fock ground state electronic configuration of 1s²2s²2p¹ (²P) is “isovalent” to the first excited ²P state of Li (but see below, the intervening 2s² pair is of significant importance). Therefore it could bind to one or two Rg atoms similarly (*vide supra*). And this is indeed the case, albeit with smaller binding energies, the D₀ (X²Π) dissociation energies ranging roughly from 20 cm⁻¹ (BNe) to 210 cm⁻¹ (BXe) [24]. Evidently, a second Rg atom can approach the BRg (X²Π) structure creating floppy BRg₂ complexes. The interaction of a Rg atom with the excited B ⁴P (2s¹2p²) state, ΔE (⁴P ← ²P) = 3.571 eV, is much stronger than previously with binding energies ranging from D_e (a⁴Σ⁻) = 412.71 cm⁻¹ (= 1.18 kcal/mol) [BHe] to as large as 3637.45 cm⁻¹ (= 10.40 kcal/mol) [BKr] [25]. The binding mechanism is identical as before, the more pronounced attractive



Scheme 5.

interaction is mainly due to the “open” structure of a ⁴P (2s¹2p²) state being more receptive to an electron pair of a Lewis base; see the vBL diagram of Scheme 5.

The same binding mechanism is observed with other “electron donors” such as CO (X¹Σ⁺), CS (X¹Σ⁺), and N₂ (X¹Σ_g⁺). Both ²P and ⁴P boron states act as Lewis acids but always the binding to the ⁴P is much stronger. The trend in the binding energies is revealing: the ²Π / ⁴Σ⁻ molecular states are bound by 1.19/76.1 kcal/mol (B–N₂), 13.3/102.8 kcal/mol (B–CO), and 50.4/141.8 kcal/mol (B–CS) with respect to B(²P/⁴P) and the ground states of N₂, CO, and CS. Notice that the ⁴Σ⁻ states of BCO and BCS are the ground states [25]. In both electronic states a dative σ bond takes place since an electron pair finds its way into an empty 2p_σ orbital of B (²P or ⁴P). Interestingly enough, it turns out that two B–L (⁴Σ⁻) species, where L = Rg, CO, CS, or N₂, which resemble the ⁴Σ⁻ state of CH, can form an acetylene like complex, L–B≡B–L ($\tilde{X}^1\Sigma_g^+$). The B₂ moiety is *in situ* in a ³Σ_g⁺ state, 4.56 eV above the X³Σ_g⁻ state [25]. Remarkably, both LB₂–L and LB≡BL bonds are stronger than the parental B–L (⁴Σ⁻) and B≡B (¹Σ_g⁺) ones, respectively [25], a result of a concerted and thus of a more effective buttoning of its constituents.

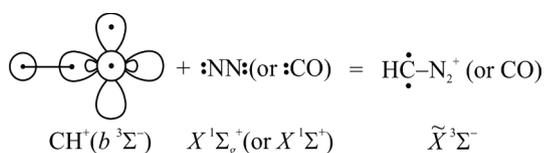
Another interesting example of the binding versatility of boron is the tetrahedral (T_d) structure of B₄H₄ [26]. Although the T_d configuration is stable with respect to four BH units and with no imaginary frequencies, it has not been experimentally observed till now. However, the global minimum of B₄H₄ is planar (C_{2v}) approximately 6 kcal/mol lower than the tetrahedral (T_d) configuration. The planar structure can be classified as an electron deficient system with only 8 electrons (provided by the four BH (a³Π) units) for six 2e⁻–2c(enter) bonds. The bond order of 8/12 = 2/3 instead of 1 is also in agreement with the system energetics; see Ref. [26] for details.

Our final example is the BH₃ molecule that has been observed only at exceedingly low concentrations but has been isolated and studied using matrix isolation techniques [15]. Its ground \tilde{X}^1A_1' state has a D_{3h} equilibrium structure with the *in situ* B atom in its ⁴P (2s¹2p²) excited state as clearly suggested by its Mulliken atomic populations, 2s^{1.14}2p_y^{0.93}2p_z^{0.93} (present calculations). Thus there is an empty 2p_x orbital perpendicular to the molecular plane giving Lewis acidity to the system. The probing of the \tilde{X}^1A_1' state of BH₃ by the simplest “ligand” possible, that is a single electron, is of interest. The BH₃⁻ anion is by symmetry of D_{3h} character with an experimentally obtained electron affinity value of 0.038 ± 0.015 eV [27] as compared to the (present) RCCSD(T)/aug-cc-pV5Z result of 0.068 eV. An H⁻ attacks the empty 2p_x boron orbital of BH₃ generating a symmetrical tetrahedral BH₄⁻ structure isoelectronic to CH₄. In both BH₄⁻ and CH₄ the central B and C atoms are found in their excited 2s¹2p² (⁴P) and 2s¹2p³ (⁵S) states, respectively. Be (2s²; ¹S) and H⁻ (1s²; ¹S) are isovalent, thus an attractive interaction is expected between BH₃ and Be. And this is indeed the case as recently discussed in Ref. [28]. As correctly pointed out by the authors there is a pair donation of the 2s² electrons to the empty 2p_x boron orbital. A similar bonding scheme occurs upon interaction of BH₃ with the Lewis bases :NN:, :CO:, and :NH₃. The theoretically predicted binding energies are around 6 (:NN:→BH₃) and 30 kcal/mol (OC:→BH₃ or H₃N:→BH₃) [29].

3.4. Carbon (C)

The carbon atom is a unique entry in the periodic table of the elements primarily due to its direct relation to all forms of life (see also Ref. [30]). The variety and versatility of organic/biochemical species is entirely due to its third excited ⁵S (2s¹2p³) atomic state, 4.18 eV above

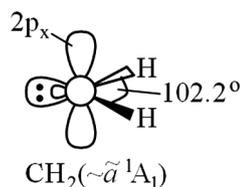
the ground 3P ($2s^22p^2$) one. For a representative example consider the formation of the two most emblematic organic molecules CH_4 (see for example Ref. [31]) and C_6H_6 (benzene). The ground 2P ($2s^22p^1$) state of C^+ is “isomorphous” to Li (2P) and isovalent to the isoelectronic B (2P), so one could expect the same type of interaction with a Rg atom. And this is indeed the case as one can see in the $(\text{HC})^+-\text{Rg}$ and $(\text{HC})^+-\text{Rg}_2$ species [32]. The CH^+ unit in both the $X^1\Sigma^+$ and $a^3\Pi$ states have enough “spare” space to accommodate electronic density from one or even two Rg atoms. The binding energies of the singlet triatomic species range from around 1 $[(\text{HC})^+-\text{He}]$ to as large as 45 kcal/mol $[(\text{HC})^+-\text{Xe}]$. The triplet triatomics, those correlating to the $a^3\Pi$ state of CH^+ , are much more bound than their singlet analogues due to the more exposed C^+ core to the incoming electron pair of Rg [32]. The idea behind the bonding mechanism is the same as before: a Lewis base (Rg, N_2 , CO) and a Lewis acid $[\text{CH}^+ (X^1\Sigma^+, a^3\Pi, b^3\Sigma^-)]$ interact attractively. Although all three CH^+ states offer space to an incoming electron pair, it is its $b^3\Sigma^-$ state, 5 eV above $X^1\Sigma^+$, that leads to the strongest interaction with either N_2 ($D_e = 164$ kcal/mol) or CO ($D_e = 200$ kcal/mol) with respect to their adiabatic products [33]. Consequently the \tilde{X} states are of $^3\Sigma^-$ symmetry as shown in the vbl diagram of Scheme 6.



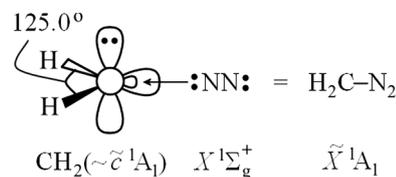
Scheme 6.

Of course the molecular species of Scheme 6 can be seen as C^+ ($2s^12p^2$; 4P) + H (2S) + N_2 (or CO). The 4P state of C^+ (isoelectronic to B) is 5.33 eV above its ground 2P state. The $X^1\Sigma^+$ CH^+ state can potentially accept the electron pairs of two Lewis bases and create a pyramidal structure. Nevertheless, it was found that $(\text{HC})^+-\text{L}_2$ has a planar C_{2v} configuration [33]. This finding can be rationalized only by considering the $B^1\Delta$ CH^+ state or equivalently the 1D atomic state of C^+ . The intrinsic bond strengths, i.e., with respect to $\text{CH}^+ (B^1\Delta) + 2\text{N}_2 (X^1\Sigma_g^+)/2\text{CO} (X^1\Sigma^+)$ amount to the astonishingly large value of 242/332 kcal/mol.

A very interesting case is the chemical bonding in diazomethane, CH_2N_2 [34] isoelectronic to H_3BN_2 , N_2NH , and N_2O (see below). Its natural components are CH_2 and N_2 but in their ground states, namely \tilde{X}^3B_1 (CH_2) and $X^1\Sigma_g^+$ (N_2), they cannot produce a closed shell \tilde{X}^1A_1 (CH_2N_2) molecule. Therefore, based solely on spin symmetry conservation arguments, we need either to excite N_2 to its triplet $B^3\Pi_g$ state [35], or CH_2 to its first excited singlet state \tilde{a}^1A_1 . The energetic cost of the $\text{N}_2 X^1\Sigma_g^+ \rightarrow B^3\Pi_g$ excitation is prohibitively large, $\Delta E = 7.39$ eV [36] while that of the $\text{CH}_2 \tilde{X}^3B_1 \rightarrow \tilde{a}^1A_1$ excitation is only $\Delta E = 9.00$ kcal/mol ($= 0.39$ eV) [37], so the adiabatic limit of the \tilde{X}^1A_1 CH_2N_2 state is $\text{CH}_2 (\tilde{a}^1A_1) + \text{N}_2 (X^1\Sigma_g^+)$. The electronic structure of the \tilde{a}^1A_1 CH_2 state is eloquently depicted by the vbl diagram of Scheme 7 clearly supporting a perpendicular N_2 attack. However, the ground diazomethane state is planar and for that to happen the σ CH_2 lone pair should somehow move to the $\sim 2p_x$ carbon orbital leaving empty its σ frame. This is mediated by the nonadiabatic interplay of the \tilde{c}^1A_1 CH_2 state; for an experimental corroboration of the proposed mechanism see Ref. [38]. Diagrammatically the molecular formation is shown in Scheme 8.



Scheme 7.

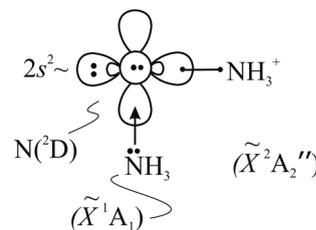


Scheme 8.

Bonding similarities occur between $\text{H}_2\text{C}\leftarrow\text{N}_2$ and $\text{H}_3\text{B}\leftarrow\text{N}_2$; recall that CH_2 and BH_3 are isoelectronic. Their only difference lies on the fact that BH_3 is a Lewis acid while in its ground state, whereas the CH_2 unit should get excited to its \tilde{a}^1A_1 state in order to acquire an analogous electronic density distribution (“acidic” behavior).

3.5. Nitrogen (N)

The CH ($X^2\Pi$) radical is isoelectronic to N with its first excited $a^4\Sigma^-$ state, the linear analogue of the ground N (4S) state, lying 5985.22 cm^{-1} ($= 17.11$ kcal/mol) above its $X^2\Pi$ state [36]. Similarly, CH^+ and N^+ (1D) are isoelectronic and the $X^1\Sigma^+$ CH^+ state is isomorphic to the first excited N^+ (1D) state ($\Delta E(^1D\leftarrow^3P) = 1.888$ eV). Based on that resemblance we can argue that N^+ (1D) should exhibit a similar chemical behavior upon interaction with an electron donor. This is indeed the case in N_5^+ ($=\text{N}(\text{N}_2)_2^+$) (\tilde{X}^1A_1), $\text{N}(\text{CO})_2^+$ (\tilde{X}^1A_1), $\text{N}(\text{Rg})_2^+$ and partly true in $\text{N}(\text{NH}_3)_2^+$ (\tilde{X}^1A_1) [39]. Each N_2 ($X^1\Sigma_g^+$), CO ($X^1\Sigma^+$), and Rg ($=\text{He, Ne, Ar, Kr; } ^1S$) species offer one electron pair to the empty $\approx 2p$ orbitals of N^+ (1D), thus two such species form two dative bonds. It should also be said that N_5^+ and $\text{N}(\text{CO})_2^+$ have been isolated experimentally in 1999 [40,41]. No doubt the cross molecular ions like NXY^+ , for instance, $(\text{N}_2)\text{N}^+(\text{CO})$, should exist as well. In the case of NH_3 though and due to the much higher ionization energy of N (4S) versus NH_3 the bonding is of mixed covalent and dative character, see Scheme 9 and Ref. [39] for more details.



Scheme 9.

Another interesting and “puzzling” hypervalent molecule is hydrogen azide, N_3H (N_2-NH), a closed shell species whose ground state is of \tilde{X}^1A' symmetry. Since N_2 ($X^1\Sigma_g^+$) is a “robust” closed shell molecular entity with its first excited $A^3\Sigma_u^+$ state lying about 6.2 eV [36] higher, the only way to obtain a singlet N_3H molecule is through a singlet NH radical, see Fig. 1. The N_3H is formed through a dative σ bond when the electron pair of N_2 finds its way to an empty $2p_x$ space of the first excited $a^1\Delta$ NH state at $12\,596\text{ cm}^{-1}$ ($= 36.0$ kcal/mol) higher [36]. The ground state interaction energy with respect to its adiabatic products $\text{N}_2 (X^1\Sigma_g^+) + \text{NH} (a^1\Delta)$ is $D_e = 51.7$ kcal/mol (present calculations, MRCI/cc-pVTZ). The electronic structure of the $\text{NH} (a^1\Delta)$ radical implies that only a perpendicular N_2 attack is possible, see Scheme 10, and indeed the NNH angle is close to 108° .

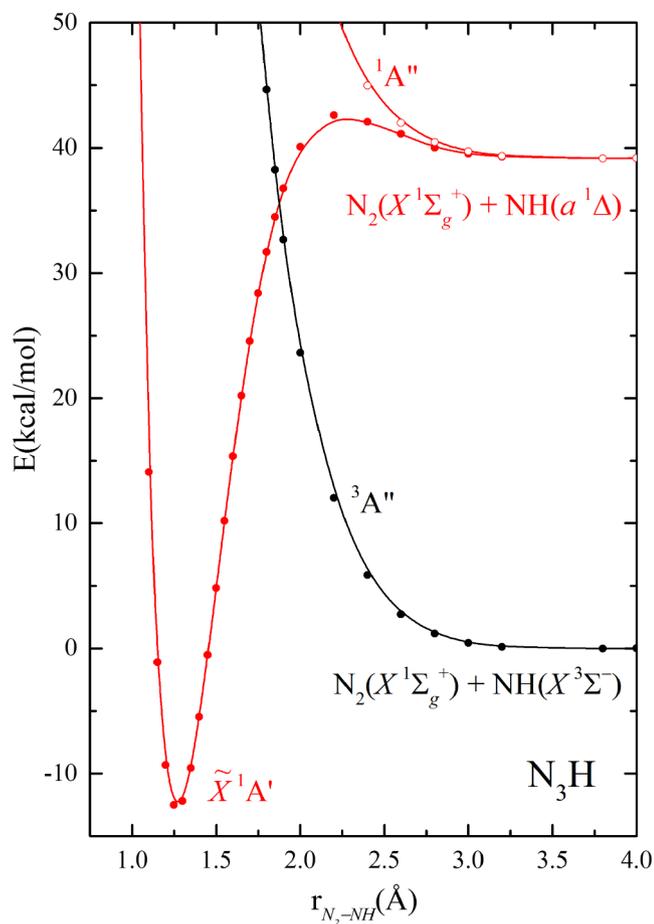
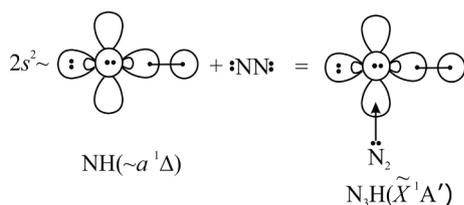


Fig. 1. MRCl/cc-pVTZ potential energy curves of the $N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-, a^1\Delta)$ interaction. The equilibrium parameters of the $N_aN_bN_cH(\tilde{X}^1A')$ state are $r_{N_aN_b} = 1.136$, $r_{N_bN_c} = 1.247$, and $r_{N_cH} = 1.018$ Å; $\angle N_aN_bN_c = 108.3$ and $\angle N_bN_cH = 171.6^\circ$.



Scheme 10.

The physical and structural properties of N_3H are in complete harmony with the proposed bonding mechanism. Consider also that N_2-NH is isoelectronic to both N_2-CH_2 and N_2-BH_3 since NH is isoelectronic to both CH_2 and BH_3 . All three systems interact attractively in a similar fashion as expected and in accordance to the general Lewis “acid–base” concept with one or more excited states of the “central” atom or unit.

3.6. Oxygen (O)

The participation of oxygen in a huge number of molecules of all kinds makes the understanding of its chemistry of pivotal importance. It has a Hartree–Fock electronic ground state valence configuration of $2s^22p^4$ (3P), “isomorphic” to $C(2s^22p^2, ^3P)$ with identical symmetries for the first (1D) and second (1S) excited states but with higher excitation energies; $\Delta E(^1D \leftarrow ^3P) = 1.958$ (O)/ 1.260 (C) and $\Delta E(^1S \leftarrow ^3P) = 4.180$ (O)/ 2.680 (C) eV. Notice that the $\Delta E(O)/\Delta E(C)$ ratios are practically identical, $1.958/1.260 = 1.55$ ($^1D \leftarrow ^3P$) and $4.180/2.68 = 1.56$ ($^1S \leftarrow ^3P$).

In connection with the previously studied species, N_2-BH_3 , N_2-CH_2 and N_2-NH , another isoelectronic molecule is nitrous oxide, N_2-O . Recall that the ground states of $CH_2(X^3B_1)$ and $NH(X^3\Sigma^-)$ are to be contrasted with the 3P state of O projected in the corresponding symmetry axis.

Once again based on both spin (angular momentum) symmetry conservation arguments and our analysis on the bonding nature of the above isoelectronic species, we should expect a bonding mechanism similar to the one encountered previously. A singlet O atom is needed and once found in this excited state a σ dative bond is formed, according to the vBL icon shown in Scheme 11; see also Fig. 2.

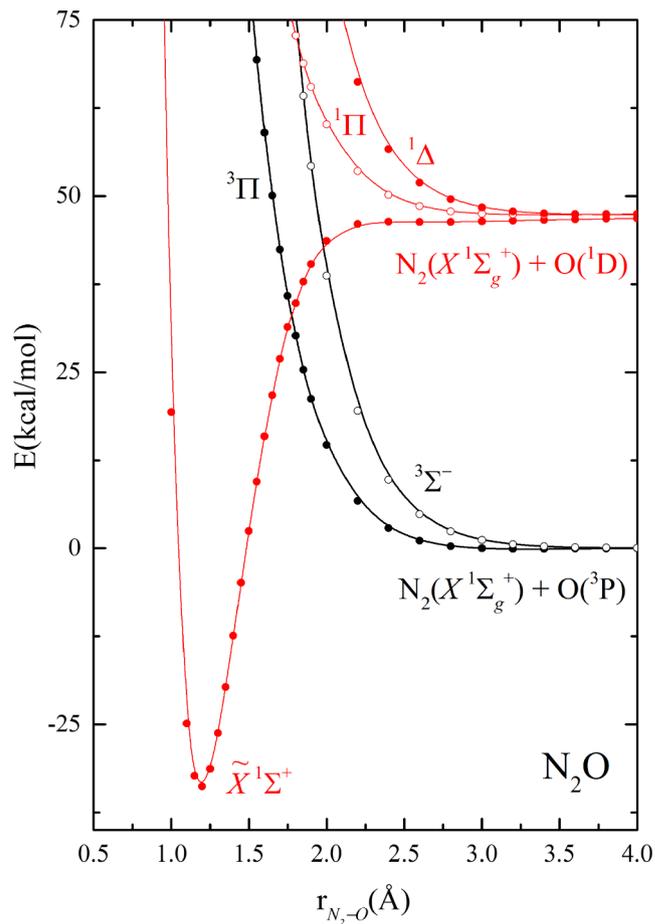
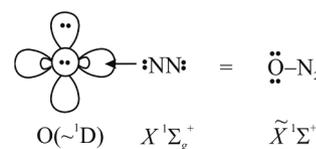


Fig. 2. MRCl/cc-pVTZ potential energy curves of the $N_2(X^1\Sigma_g^+) + O(^3P, ^1D)$ interaction. The equilibrium parameters of the $N_2O(\tilde{X}^1\Sigma^+)$ state are $r_{NN} = 1.132$ and $r_{NO} = 1.188$ Å.



Scheme 11.

The interaction is quite significant with a binding energy amounting to 88.3 kcal/mol with respect to its adiabatic fragments $N_2(X^1\Sigma_g^+) + O(^1D)$ (present calculations, RCCSD(T)/cc-pVTZ). Once again, the $:NN:\rightarrow O$ molecule is hypervalent! A second $O(^1D)$ atom can also interact attractively with the other end of $:NN:\rightarrow O$ in a similar way. The $\tilde{X}^1\Sigma_g^+$ state of $O\leftarrow:NN:\rightarrow O$ is bound by 60.4 kcal/mol at the RCCSD(T)/cc-pVTZ

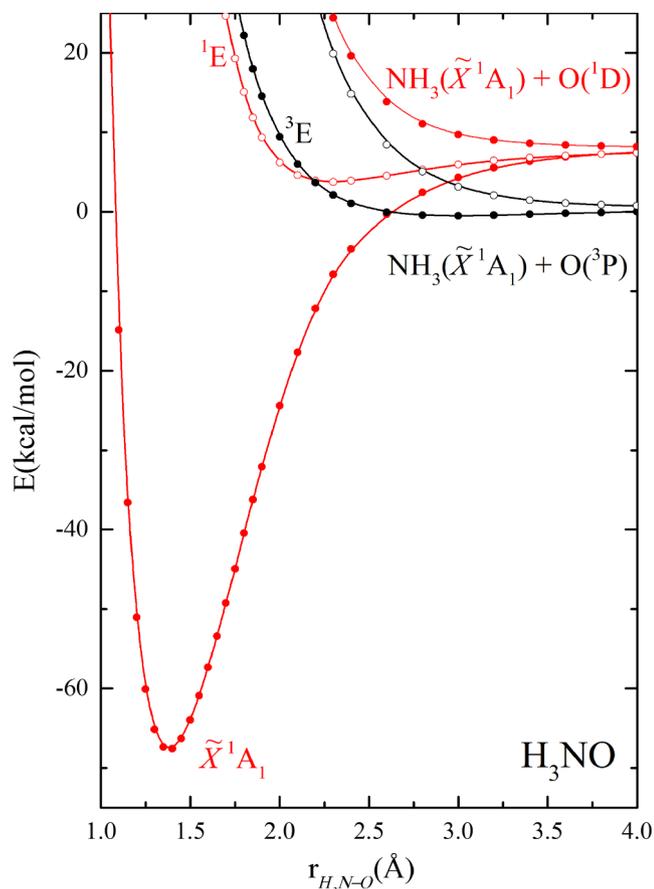
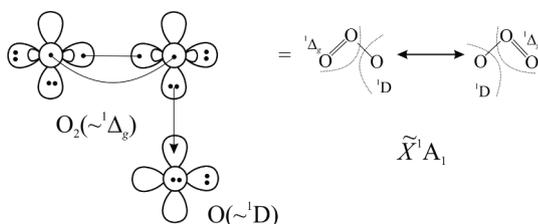


Fig. 3. MRCl/cc-pVTZ potential energy curves of the $\text{NH}_3(\tilde{X}^1A_1) + \text{O}(^3P, ^1D)$ interaction. The equilibrium parameters of the $\text{H}_3\text{NO}(\tilde{X}^1A_1)$ state are $r_{\text{NH}} = 1.029$, $r_{\text{NO}} = 1.366$ Å, and $\angle \text{HNO} = 112.9^\circ$.

computational level (present calculations) with respect to $\text{N}_2\text{O}(\tilde{X}^1\Sigma_g^+) + \text{O}(^1D)$ while with respect to $\text{N}_2(X^1\Sigma_g^+) + 2\text{O}(^3P)$ is bound by 46.7 kcal/mol. At the RCCSD(T) (MRCl)/cc-pVTZ level the geometry of $\text{O}-\text{N}_2-\text{O}$ is $r_{\text{NN}} = 1.225$ (1.217) and $r_{\text{NO}} = 1.124$ (1.120) Å as compared to the MRCl values of $r_{\text{NN}} = 1.132$ and $r_{\text{NO}} = 1.188$ Å of N_2-O ; see Fig. 2.

The same binding philosophy applies also to other Lewis base species such as, for instance, $\text{NH}_3(\tilde{X}^1A_1)$ or $\text{PH}_3(\tilde{X}^1A_1)$ [42]. The N: (P:) $2s^2(3s^2)$ pair finds its way to an empty $2p$ orbital of $\text{O}(^1D)$ resulting to the formation of a harpoon like σ bond stabilizing the $\text{H}_3\text{N}:\rightarrow\text{O}$ ($\text{H}_3\text{P}:\rightarrow\text{O}$) complex by 83.9 (153.0) kcal/mol (present calculations, RCCSD(T)/cc-pVTZ), see Fig. 3 ($\text{H}_3\text{N}:\rightarrow\text{O}$).

Without any doubt the excitation of $\text{O}(^3P)$ to $\text{O}(^1D)$ creates the



Scheme 12.

necessary “space” that “houses” the electronic density of an incoming electron pair. A series of well known and common molecules interact attractively in a similar way. A representative and very interesting example is ozone, O_3 . It is a singlet closed shell molecule featuring an isosceles C_{2v} equilibrium geometry. Although upon dissociation the \tilde{X}^1A_1 state goes adiabatically to $\text{O}_2(X^3\Sigma_g^-) + \text{O}(^3P)$ its diabatic limit is $\text{O}_2(a^1\Delta_g) + \text{O}(^1D)$, therefore it was suggested that $\text{O}_3(\tilde{X}^1A_1)$ is bound through a dative bond between two singlet excited fragments, $\text{O}_2(a^1\Delta_g)$ and $\text{O}(^1D)$ [23]; see the vBL of Scheme 12 (the resonance shown is by symmetry). Please note that both the *in situ* entities, dioxygen and oxygen, are in their first excited states $a^1\Delta_g$ and 1D , respectively. It is worth mentioning at this point that this counter intuitive and very interesting electronic distribution of O_3 , is in agreement with certain of its physical properties as discussed in the book by Greenwood and Earnshaw, see Ref. [15].

Incidentally these findings on O_3 shed new light on its electronic structure believed to be an open singlet [43]; but see also Ref. [44]. As “unusual” as it may appear, the participation of the *in situ* $\text{O}(^1D)$ in the ground ozone state is rather common in many ordinary molecules such as, sulfuric H_2SO_4 [(HO) $_2$ SO $_2$] and hyperchloric acids HClO_4 [(HO)ClO $_3$]; see Ref. [45]. In the sulfuric acid two OH ($X^2\Pi$) units bind covalently to the singly occupied $3p$ orbitals of S ($3s^2 3p_y^2 3p_x^1 3p_z^1$; 3P) while the remaining two O atoms being excited to their 1D atomic states bind to S(OH) $_2$ by accepting the electronic density of the ($\approx 3s$) 2 and ($\approx 3p_y$) 2 pairs of the *in situ* S atom. The same mechanism prevails in HClO_4 [= (HO)ClO $_3$]. An OH ($X^2\Pi$) binds covalently to the singly occupied $3p_z$ orbital of Cl ($3s^2 3p_x^2 3p_y^2 3p_z^1$; 2P) whereas three $\text{O}(^1D)$ excited atoms bind datively to three Cl “observer” pairs, Cl: $\rightarrow\text{O}(^1D)$. Certainly the same bonding mechanism holds to the whole of series of the oxoacids of the halogens, for instance HOCl: $\rightarrow\text{O}$ and HOCl: $\rightarrow(\text{O})_2$, or HOBrO $_2$ and HOBrO $_3$, or HOIO $_2$ and HOIO $_3$ (see Ref. [15], p. 853). All these molecules, “hypervalent” of course, cause bewilderment as far as their X-(O) $_n$ (X = Cl, Br, I) bonding is concerned. The fact that corresponding fluoro oxoacids have not been isolated is the result of a negative energy interplay between the O excitation ($^1D \leftarrow ^3P$) and the harpoon like bonding energy F: $\rightarrow\text{O}$. The oxidizing power of agents such as $\text{C}_6\text{H}_5\text{IO}_n$ ($n = 1, 2, 3$) is due to the *in situ* 1D oxygen atom(s) [46]. The same bonding scenario exists as well in phosphoric acid, H_3PO_4 [= (OH) $_3$ PO]. Three single covalent bonds between three OH ($X^2\Pi$) units and the three $3p$ singly occupied orbitals of P ($3s^2 3p_x^1 3p_y^1 3p_z^1$; 4S) are formed while a fourth $\text{O}(^1D)$ atom receives the ($\approx 3s$) 2 electronic density of the P atom, (HO) $_3$ P: $\rightarrow\text{O}(^1D)$ [45].

The electronic structure of the bent C_{2v} ClO $_2$ radical (\tilde{X}^2B_1 ; $\angle \text{OClO} \approx 118^\circ$) can be naturally rationalized along the same lines of thinking. Although it has a C_{2v} geometry the two O atoms bind differently to Cl (2P), the restoration of the C_{2v} symmetry is due to the resonance (by symmetry) of the two C_s structures as is also the case in ozone. In the ClO ($X^2\Pi$) radical there is a regular σ bond between Cl (2P) and O (3P) with the spin defining electron density residing on O. A second oxygen atom binds datively to one of the electron pairs of Cl through its 1D excited state, see Fig. 4. Although ClO $_2$ dissociates to ClO ($X^2\Pi$) + $\text{O}(^3P)$ the whole process goes on with a barrier due to an avoided crossing with a state coming down from the ClO ($X^2\Pi$) + $\text{O}(^1D)$ asymptote (present calculations, MRCl/cc-pVTZ). The bonding situation is schematically given by the vBL diagram of Scheme 13.

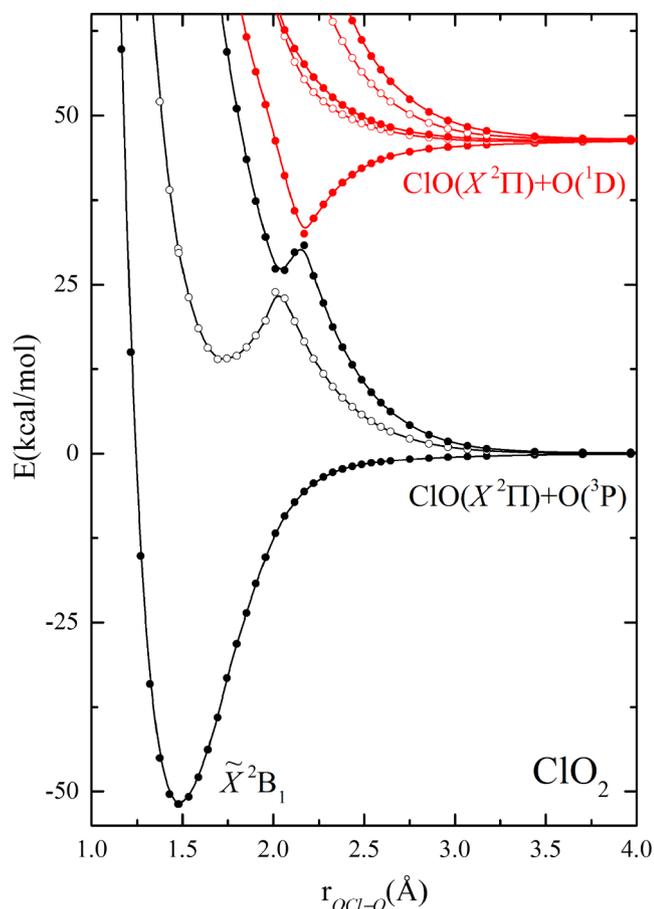
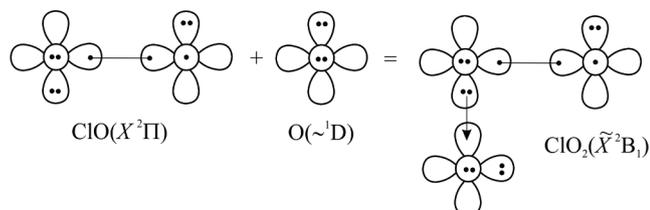


Fig. 4. MRCl/cc-pVTZ potential energy curves of the ClO ($X^2\Pi$) + O (3P , 1D) interaction. The equilibrium parameters of the ClO₂ (\tilde{X}^2B_1) state are $r_{\text{ClO}} = 1.477 \text{ \AA}$ and $\angle \text{OCIO} = 118.1^\circ$.



Scheme 13.

It is perhaps useful to remind the reader that the spin density defining the symmetry of ClO₂ resides on both O atoms as it is happening in a variety of similar systems, with symbols $\text{O} \leftarrow \text{Cl} - \dot{\text{O}} \leftrightarrow \dot{\text{O}} - \text{Cl} \rightarrow \text{O}$, $\angle \text{OCIO} \approx 118^\circ$. Two more O (1D) atoms attack ClO₂ the same way in order to form the ClO₄ radical whose binding mode is essentially the same as in HClO₄; see above.

Another class of “peculiar” molecules comprises FClO_x ($x = 1-3$) and Cl₃PO, see Ref. [47]. In all of the above molecules the O (1D) atoms receive an electronic density from either Cl (FCl) or P (Cl₃P). Needless to mention the similarities of the $\text{O} \leftarrow \text{NH}_3$, $\text{O} \leftarrow \text{P}(\text{OH})_3$, and $\text{O} \leftarrow \text{PCl}_3$ binding mechanisms.

Xenon (Xe) compounds can be thought of as an exception to the “nobility” of the atom. In particular its oxides, XeO_n ($n = 1-4$), were synthesized in the early sixties (see Ref. [48] for more details). The binding mode is again the same as before. The oxygen atom(s) excited in their 1D state form dative bonds through the donation of the electronic density of the four Xe electron pairs, $5s^2 5p^6$, to the empty $2p$ O (1D) orbitals. The RCCSD(T) D_0 binding energies of XeO_n with respect to Xe (1S) + n O (1D) are 33.7 ($n = 1$), 92.2 ($n = 2$), 180.2 ($n = 3$), and

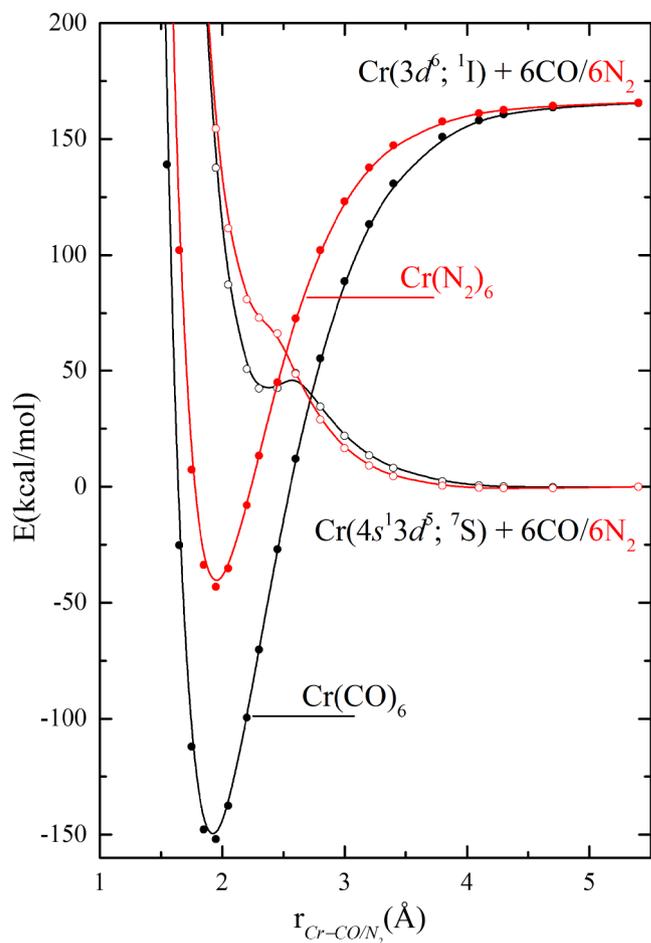


Fig. 5. RCCSD(T)/cc-pVTZ potential energy curves of the Cr + 6CO ($\tilde{X}^1\Sigma^+$)/6 N₂ ($X^1\Sigma_g^+$) interaction.

251.4 ($n = 4$) kcal/mol [48]. See also Refs. [49] and [50] for the “metastable” molecule ArO₄ isoelectronic to [ClO₄⁻].

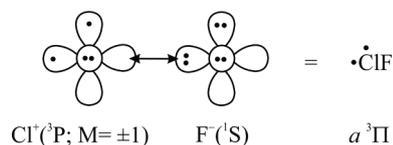
3.7. Chromium (Cr)

Bonding in transition metal compounds is a fascinating and perhaps a “mysterious” subject in terms of how the constituent fragments bind relatively strongly together. The high density of their low-lying excited states grants them a binding versatility that is reflected in their catalytic properties. The generally accepted bonding mechanism has been introduced almost 70 years ago by Dewar [51] and by Chatt and Duncanson [52] and relies on a synergistic model that involves the formation of a σ bond through donation of electron density from the ligand to a suitably directed metal hybrid orbital, and the accompanying back donation from a filled d metal orbital into a vacant π^* orbital of the ligand. Carbon monoxide (CO; $X^1\Sigma^+$) is undoubtedly the most famous of all ligands in inorganic chemistry and it is considered to be the prototype of π -back donation. Although not explicitly said it is tacitly assumed that all six valence $4s^1 3d^5$ electrons of Cr (7S) are “zipped” together in electron pairs in the d shell in a “virtual” singlet atomic state. Therefore six CO moieties approach the “hybridized” metal from its carbon end transferring electronic pair density to the remaining six empty $4s 3d 4p$ hybrid orbitals filling them all and resulting to the stable Cr(CO)₆ complex similar to a Kr atom. This is the origin of the celebrated 18 e^- rule that is obeyed by all but the V(CO)₆ of the 3d transition metal mononuclear carbonyls, *i.e.*, Cr(CO)₆, Fe(CO)₅, and Ni(CO)₄. This 18 e^- rule is *mutatis mutandis* analogous to the 8 e^- rule followed by the main group elements. The latter offer the “space” to four electron pairs through the valence $2s$ and $2p$ orbitals while the

3d-transition metals provide the “space” to nine electron pairs through the 4s, 4p, and 3d atomic orbitals.

In a detailed and meticulously crafted study of $\text{Cr}(\text{CO})_6$ Davidson and coworkers [53–55] ascribed the bonding primarily to the electrostatic attraction owing to the interpenetration of the σ carbon ($:\text{CO}$) lone pairs with the metal 3s, 3p, and 3d orbitals and not through mixing of the CO σ orbitals with the Cr empty valence orbitals. Needless to say that the Cr metal is excited into a (*in situ*) singlet spin state in order to conform to an overall singlet state and to leave some *d* orbitals empty to minimize the repulsive effects with the incoming ligand electron pairs.

We have presently studied the isoelectronic $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{N}_2)_6$ complexes by simultaneously approaching six CO or six N_2 units in an O_h symmetrical fashion; see Fig. 5 [RCCSD(T)/cc-pVTZ]. In the case of the carbonyl complex it is clear that the bonding is entirely due to a d^6 singlet coupled Cr configuration. The electrostatic character of the bonding is also mirrored in the Mulliken valence CASSCF populations of the Cr center, i.e., $4s^{0.53}3d^{5.17}4p^{0.40}$. The empty *d* orbitals of the d^6 singlet coupled Cr configuration are not being populated by the incoming CO lone pairs. Similarly in the $\text{Cr}(\text{N}_2)_6$ case the corresponding atomic distributions are $4s^{0.17}3d^{5.31}4p^{0.27}$. In both cases the three electron metal pairs are localized on the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ atomic orbitals in order to minimize the electronic density on the *x*, *y*, and *z* axes along which the CO or N_2 approach the metal. The $\text{Cr}(\text{CO})_6$ system is stabilized by ≈ 150 kcal/mol at the RCCSD(T)/cc-pVTZ level (or 25 kcal/mol per bond) with respect to the ground state fragments, while the $\text{Cr}(\text{N}_2)_6$ is marginally bound (see Fig. 5) due to the intrinsically weaker electrostatic attraction between Cr and N_2 . The O_h symmetric dissociation of both $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{N}_2)_6$ to their diabatic fragments at the single configuration



Scheme 14.

RCCSD(T) level reveals clearly the absence of any covalent bonding. It is rather clear that the bonding in $\text{M}(\text{CO})_n$ and similar complexes, where M is a 3d-transition metal element, is simply of electrostatic nature. Previous assumptions about “back donation” are untenable.

3.8. ClF_3 , SF_6 , and borazine

ClF_3 is considered to be one of the most reactive compounds known and reacts violently even with substances thought of as inert for example asbestos. Its explosive properties have been recognized quite early as it was used in incendiary bomb attacks in UK cities during the Second World War [15]. Its parental molecule is evidently ClF, the most robust from the interhalogen diatomics. But how do two F (^2P) atoms bind to ClF in order to form a closed shell ClF_3 molecule? ClF_3 is formed through the first excited $a^3\Pi$ state of ClF [56] (see Fig. 6) featuring both the spin defining electrons on the Cl atom. The $a^3\Pi$ state lies $18\,826.4\text{ cm}^{-1}$ ($=53.83\text{ kcal/mol}$) above the $X^1\Sigma^+$ state [36,56]. Although adiabatically ClF_3 dissociates to $\text{ClF}(X^1\Sigma^+) + 2\text{F}(^2\text{P})$, its diabatic route is through the ClF ($a^3\Pi$) state via an avoided crossing at around 2.1 \AA resulting in a barrier of 41 kcal/mol at the MRCl/cc-pVTZ computational level (present calculations). This bonding mechanism has been suggested by Chen et al. [57] as part of the recoupled pair bonding theory introduced by Woon and Dunning in 2009. [58] According to their study [57] the ClF ($a^3\Pi$) is formed when a Cl $3p^2$ electron pair aligned with the internuclear axis gets decoupled so that a quartet spin state is realized for Cl and then a σ bond is formed with a F (^2P) atom. Our MRCl wavefunction indicates an electrostatic σ interaction between a $\text{Cl}^+(^3\text{P})$ and $\text{F}^-(^1\text{S})$ diagrammatically shown in the vBL of Scheme 14.

The electrostatic nature of the ClF bond explains also the explosiveness of ClF_3 . Based on the above vBL diagram we can easily understand the formation of ClF_3 . Two F (^2P) atoms form two single bonds with the two high spin electrons residing on Cl creating a quasi T-shaped C_{2v} structure. Indeed the RCCSD(T)/cc-pVTZ optimized geometry ($r = 1.605$ and 1.698 \AA , $\angle \text{FCIF} = 87.1^\circ$) is in full agreement with the geometry dictated by the electronic structure of ClF ($a^3\Pi$) and corresponding experimental results.

SF_6 is undoubtedly one of the most famous hypervalent molecules. Its bonding history is nicely narrated in Ref. [58] along with a proposed formation mechanism based on the recoupled pair bonding theory. The founding stone is the $^4\Sigma^-$ state of SF that according to Ref. [58] results from “... a decoupling of the singlet coupled S $3p_z$ pair of electrons and a subsequent recoupling of one of these electrons with the electron in the F $2p_z$ orbital to form a new covalent bond pair.” Then the three high spin electrons can form three single bonds with three F (^2P) atoms in order to form SF_4 . Then the recoupling of the S $3s^2$ electrons results into the formation of SF_6 by adding two more F atoms. In a recent study [59] we have shown that the bonding in both SF ($^4\Sigma^-$) and SF_6 is ionic in nature and rather not the result of any recoupling.

Borazine, $\text{B}_3\text{N}_3\text{H}_6 = (\text{BH})_3(\text{NH})_3$, a planar arrangement of its constituent fragments, is isoelectronic to benzene featuring as well 6 π electrons but practically deprived of aromatic characteristics. It is known also as “inorganic benzene” and has been studied extensively; see Ref. [60] for details. Contrary to benzene the 6 π electrons are localized in pairs on the N atoms so the question of how do the BH and NH units bind together was of central importance. If one wants to understand borazine one has to understand the binding of BH and NH motifs in their various excited states. It was shown in Ref. [60] that the first excited $a^3\Pi$ (BH) and $A^3\Pi$ (NH) states, 30.4 and 87.9 kcal/mol

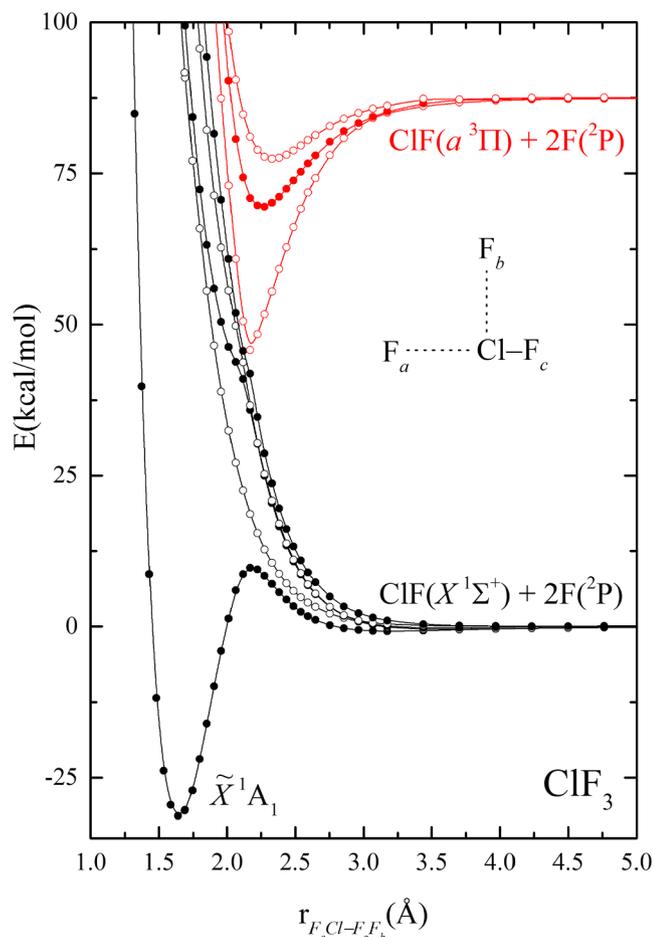
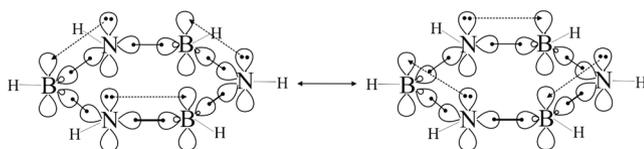


Fig. 6. MRCl/cc-pVTZ potential energy curves of the $\text{ClF}_c(X^1\Sigma^+, a^3\Pi) + 2\text{F}_{a,b}(^2\text{P})$ interaction. The equilibrium parameters of the quasi T-shaped $\text{ClF}_3(\tilde{X}^1A_1)$ state are $r_{\text{ClF}_{a,c}} = 1.690$, $r_{\text{ClF}_b} = 1.595\text{ \AA}$, and $\angle \text{F}_{a,c}\text{ClF}_b = 86.9^\circ$.

above their respective ground ones, combine together to form the ground state borazine molecule; see vbl Scheme 15.



Scheme 15.

4. Epitome

Armed with the indisputable tenets of chemistry and physics that molecules are bound conglomerates of nuclei and electrons described by the Schrödinger equation, we have tried to exorcize the definition–concept of hypervalency as redundant at least the way it is commonly used by most practitioners of chemistry, not for communication purposes but as an “explanation–understanding” of the bonding. Chemistry is indeed a very complicated field of natural sciences and deeply enmeshed with life itself. Therefore chemists were obliged very early to introduce a plethora of empirical ideas, useful in the time of their introduction and perhaps useful even today, but not founded within the corpus of our Physical Laws. We do not propose to explain the physiology of smelling employing quantum mechanics (at least not now; but see Ref. [61]), we have to forsake, however, certain ideas clearly of historical value but obsolete by now.

We would like to emphasize that “hypervalent” molecules are not an exception to the “traditional rules” of chemistry, on the contrary almost the vast majority of molecules conform to the Musher definition. At this point we have to repeat what we wrote in a recent publication [47].

“For example the simplest of all organic molecules, CH₄, could be clearly considered of hypervalent nature. Indeed, by bonding to H (²S) atoms to the ³P ground state of C, a closed shell species is obtained, namely CH₂ (¹A₁), with no further ability for binding. To add two more H (²S) atoms we can involve either the ³B₁ state of CH₂ originating from the ⁵S state of C atom ≈ 97 kcal/mol higher, or equivalently, to couple into a singlet four H (²S) atoms to the ⁵S state, the energy profit for both cases being ≈ 300 kcal/mol. The latter process is usually called sp³ hybridization.”

Four years later exactly the same conclusion was reached by the Dunning group [62]. If CH₄ is hypervalent, certainly all hydrocarbons saturated or not are hypervalent as well. Recall that H₂C=CH₂, HC≡CH, and C₆H₆ (benzene) can be thought of as made by their natural units CH₂ (³B₁) and CH (⁴Σ⁻), related directly to the ⁵S carbon state. Therefore all proteins are hypervalent molecules, that is practically all organic and biological molecules!

Our previous quotation [47] ends with the word “hybridization” well known to every chemist and used as a passe partout to “explain” the structure of the simplest of molecules and directly related to hypervalency as previously discussed. It is remarkable what R.P. Feynman has to say in explaining the structure of H₂O and NH₃ and related molecules in the third volume of “The Feynman Lectures on Physics” more than half a century ago (vol. III, p. 19–17 and 19–18) [63]. He follows the fundamental rules of Nature, *i.e.*, simplicity, the electronic distribution of atoms in space according to quantum mechanics, and that two electrons coupled into a singlet refer to a single “chemical” bond. In verbatim “Consider then what happens in H₂O. Each of the two hydrogens are willing to share an electron with the oxygen, helping the oxygen to fill a shell. These electrons will tend to go into the “x” and “y” vacancies. So the water molecule should have the two hydrogen atoms making a right angle with respect to the center of the oxygen. The angle is actually 105°. We can even understand why the angle is larger than 90°. In sharing their electrons the hydrogens end up with a net positive charge. The electric repulsion “strains” the wave functions and pushes the angle out to 105°. The same situation occurs in H₂S. But because the sulfur atom is larger, the two hydrogen atoms are farther apart, there is less repulsion, and the angle is only pushed out to about 93°. Selenium is even larger, so in H₂Se the angle is very nearly 90°”.

He follows the same line of thinking in explaining the geometry of NH₃, PH₃, and AsH₃. No mention to hybridization or, as a “modern” chemist would put it to the VSEPR (valence shell electron pair repulsion) “theory”, another redundant model but very popular nowadays. We completely agree with Feynman corroborated absolutely by the experimental results as shown below (see *e.g.* Ref. [15]): ∠ H₂O = 104.5°, ∠ H₂S = 92.1°, ∠ H₂Se = 91°, ∠ H₂Te = 90° and ∠ HNH (NH₃) = 107.8°, ∠ HPH (PH₃) = 93.6°, ∠ HASH (AsH₃) = 91.8°, ∠ HSbH (SbH₃) = 91.3°, and ∠ HBiH (BiH₃) = 90.5° [64].

The above discussion on bonding of the H₂X (X = O, S, Se, and Te) and H₃Y (Y = N, P, As, Sb, and Bi) molecules is not related to hypervalency but shows unequivocally how by avoiding simplicity we create unnecessary havoc. In a nutshell, hypervalency is bonding achieved via excited state atoms or through excited state “units”.

We conclude by saying that chemistry is like a jigsaw puzzle for grownups and consequently it is fun. As in puzzles there are building blocks, the atoms, but unlike puzzles’ building blocks, the atoms are not rigid but quantum entities (quantons) that display a remarkable agility through its various atomic states. So their chemical association does not furnish only one construction as in puzzles but, in principle, myriads.

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