Blooming and Decline of the Two-electron Bond 1916-1984*

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Abstract

Coordination numbers N between 5 and 16 in inorganic and organo-metallic compounds are discussed, and special cases of the Lewis paradigm, such as the hybridization hypothesis and the Kimball model, are critically compared with the more recent cross-fertilization between quantum chemistry and experimental studies of optical and photoelectron spectra. The relation between acidity and oxidizing character is shortly analyzed.

Lewis [1] suggested that the typical chemical bond is effectuated by two electrons, that well-behaved elements have 8 outer electrons (either shared as electron pairs with adjacent atoms, or remaining on the atom as lone-pairs) and, if the coordination number N is at most 4, then $2N$ among the 8 electrons form single bonds (double and triple bonds being assigned 4 or 6 electrons). In view of this proposal being made eight years before Stoner rationalizing the Periodic Table by nl-shells accomodating at most $(4l+2)$ electrons, it would be unfair to criticize the Periodic Table seen on the walls of American barber shops with electrons clustered two and two on four of the corners of a cube (selecting a regular tetrahedron). It must also be admitted that aliphatic organic compounds, and in particular the almost non-polar alkanes, are admirably described by this model. However, the problems appear at a very fundamental level. Children are indoctrinated that «all compounds consist of molecules». This is certainly true in the gaseous state at reasonable temperature and pressure (say, below 1000°C and 20 atm.) but the majority of inorganic compounds in condensed matter (liquids; vitreous, amorphous and crystalline solids) do not contain distinct molecules, and a large part are perceptibly non-stoichiometric. The modification of the Lewis electron-pair description by amendments and exceptional inorganic cases reminds one about the Ptolemaïc epicycles attempting to save the geocentric system.

Quantum chemistry has the last 50 years divided in a rather difficult «vertical» area and an exceedingly difficult (and probably in part impossible) «adiabatic» area. The «vertical» area grew out of the major triumph of early quantum mechanics, the line-spectra of monatomic entities [2,3] and is concerned with optical excitations studied by absorption [4-6] and luminescence [7-9] spectra, and with photo-electron spectra [10-13]. The word «vertical» refers to the potential curves of a diatomic molecule. Both the experimental techniques of optical excitation and photolectron ionization follow Franck and Condon's principle of nuclei staying immobile during the quantum jump between the electronic wave-functions, and both have provided strong and quite unexpected evidence for the

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utility of molecular orbital (M.O.) configurations in oligoatomic chromophores, involving both low-lying (partly filled or empty in the groundstate), highest filled (H.O.M.O.) and penultimateM.O. (previously considered as calculational artifacts). As far goes inner shells, condensation of atoms to metallic elements, or chemical bonding, typically modifies the ionization energies by some 5 to 10 eV (higher than usual bond dissociation energies). The relations between isoelectronic series with $K = (Z\text{-}z)$ electrons (Z being the atomic number and z the oxidation state) and X-ray spectra first emphasized by Kossel in 1916 [14-16] are not only determined by the fractional atomic charges and by the Madelung potential due to the surrounding ions [5,17] but to a comparable extent by relaxation effects [12,18] closely related to the idea of chemical polarizability [19]. Chemical reactions are «adiabatic» in the sense that the n nuclei move, and a major difficulty for quantum chemistry is that the motion takes place on (3n-5)-dimensional potential surfaces (since six degrees of rotational and translational freedom are removed in the Born-Oppenheimer approximation, when n is at least 3).

Today, it is appropriate to say that chemistry is the mutual adaptation of the electronic density to a set of nuclei with charges $Z_1, Z_2, \ldots.$ moved to (relative or absolute) minima of energy. The internal constitution of nuclei would have very little relevance for chemists, if it was not for the recent evidence [20] that niobium may contain unsaturated quarks to the extent of one per 10^{20} units of atomic weight (or 6000/g). Such carriers of fractional charge [21-25] intercalates new «elements» with ($Z \pm 1/3$) in the Periodic Table, which are expected to undergo strong geochemical fractionation, because they cannot be fully neutralized by electrons.

In a static description of «chemical bonds» the preliminary proposition is that an ideal gas of geometrical points has a distribution of radial probability P(r) relative to one point at origo proportional to $4\pi r^2 dr$. It is more informative to divide an observed P(r) by this factor. X-ray diffraction studies of crystalline solids indicate very closely (or exactly) the nuclear equilibrium positions, which are also found by neutron diffraction. If these two techniques are applied to liquids and glasses (or electron diffraction to gaseous molecules) it is still possible to estimate P(r) though the angular shape can no longer be determined. If we plot P(r) for a large number of instances of two nuclei Z_1 and Z_2 *it is well-known that there are no very short r occurring. A narrow, strong maximum occurs at r =* R which we take as a manifestation of a «chemical bond». The half-width of this maximum has the order of magnitude 0.1 Å, and it is not much broader than the mean dispersion at room temperature due to thermal vibrations. The peak at R is somewhat asymmetric, it is much more frequent for a «bond» to be (R + 0.2) than (R-0.2) Å. Cases of exceptionally low r (such as N_2 compared with hydrazine or azobenzene; and the two linear uranyl bonds [8] in $UO_2(O_2NO)_3^-$) frequently correspond to very low chemical reactivity. The maximum of P(r) at R is followed by a broad valley with very few examples (weak sulphur-sulphur and iodine-iodine interactions may fall in this interval, and traditionally. short hydrogen bonds FHF^- and OHO are also included, because the hydrogen atoms are difficult to localize with X-rays) before a hilly landscape of «-van der Waals contacts» starting at least 1Å beyond R. Slater [26] reactivated the idea of Braggs that atoms show a roughly constant radius in condensed matter. One smoke-screen around this question is that the ionic radius of a cation is said to bei 0.8 Å smaller than the «covalent radius» of M with the result that the observed R typically scatter only some 0.1 Å from the two kinds of M + X radii. It must be added in all fairness that the Goldschmidt ionic radii are fixed by assuming direct contact between spherical anions in NaC1-type LiI and in CaF_2-type CeO_2. It may also be noted that the Cs-Cs internuclear distance in NaCl-type CsF is much shorter than in metallic caesium, without any evidence for «intermetallic bonding» in the fluoride.

The coordination number N is not always well-defined. It is the number of «bonds» if all nearest neighbour atoms with the same Z show the same r. It is a matter of taste how much longer (say 1.10 to 1.15 R) non-equivalent bonds can be, and still be counted in N. Such cases were recently discussed [27] with emphasis on N larger than 4, providing the counterexamples to the Lewis paradigm. The most common stereochemistry for $N = 5$ is the trigonal bipyramid, though such species (like gaseous $PC1_5$) frequently disrupt (to solid $PC1_4^+PC1_6^-$). Tetragonal pyramids occur in the $K = 48$ isoelectronic TeF_5^-, IF_5, XeF_5^+ and $OXeF_4$, the vanadyl ion $OV(OH_2)_4^{+2}$, in $Cu(NH_3)_5^{+2}$, in orange $Ni(CN)_5^{-3}$ (diamagnetic $3d^8$ with $S = 0$) and green $Co(CN)_5^{-3}$($S = 1/2$) able to form a purple dimer isosteric and isoelectronic with $(OC)_5MnMn(CO)_5$ of two octahedra «glued together» whereas F_5SSF_5 is not known to monomerize to SF_5. For $N = 6$, octahedral symmetry is by far the most frequent, and as first pointed out by Werner, occurs in the majority of d-group complexes. An isoelectronic series of main-group complexes is AlF_6^{-3}, SiF_6^{-2}, PF_6^-, SF_6 and ClF_6^+. Mg(II), Al(III), Zn(II) and Ga(III) are known to form octahedral aqua ions in solution. Exceptional cases of $N = 6$ are the trigonal prism of sulphur-containing ligands [5] and the two low-symmetry sites of cubic C-type M_2O_3 (isotypic Be_3P_2 and Mg_3P_2).

Starting with $N = 7$, there is generally very little preference [28] for a given $N = 8,9,10\ldots$ nor for a definite stereochemistry for a given N. Crystalline neodymium (III) salts are known to contain $Nd(OH_2)_9^{+3}$ with the same trigonal symmetry as the rhenium (VII) complex ReH_9^{-2} but it is still not known [29] whether the aqueous Nd(III) solution contains a mixture of $N = 9$ and

8. A comparable, very careful, neutron scattering study [30] of strong calcium chloride solutions indicates a mixture ranging from $N = 10$ to 6. The six bidentate nitrate ligands are known to provide approximately icosahedral $N = 12$ in salts containing $Nd(O_2NO)_6^{-3}$, $Ce(O_2NO)_6^{-2}$ and $Th(O_2NO)_6^{-2}$.

Though only reluctantly admitted by text-books, organometallic compounds frequently show $N = 9$ to 16. The sandwich complexes (with identical M-C distances) of cyclopentadienide, benzene and cyclooctatetraenide such als $3d^6$ $Fe(C_5H_5)_2$ and $Co(C_5H_5)_2^+$ have $N = 10$, the $3d^6$ $Cr(C_6H_6)_2$ and $3d^5(S = 1/2)$ $Cr(C_6H_6)_2^+$ (readily obtained by oxidation) $N = 12$ (like the mixed $4d^6$ complex involving the tropylium cation $(C_5H_5)Mo(C_7H_7))$, and $Ce(C_8H_8)_2^-$, $Th(C_8H_8)_2$, $U(C_8H_8)_2$ and $Am(C_8H_8)_2^-$ all have $N = 16$. The same high N value is known from many U(IV) complexes $(C_5H_5)_3UX$ with one unidentate X^-, and from the cyclohexylisonitrile adduct $(C_5H_5)_3YbCNC_6H_{11}$.

The hybridization theory contains the Lewis paradigm as an essential assumption, as previously discussed [31,32]. At this point, the light elements from beryllium to fluorine are in a more favourable position than all the subsequent elements in the sense that the 2s and 2p radial functions to a much better approximation can be put outside a parenthesis (to be multiplied by a linear combination of angular functions belonging to $l = 0$ and 1). The physical reason behind this result is the tiny atomic core of only two electrons almost coinciding with the nucleus. It is probably a question of relative atomic size that NF_4^+ and ONF_3 are known (but not NF_5) and it should not be neglected that oxygen and nitrogen have $N = 6$ in NaCl-type MgO, MnO, NiO, CdO and LaN and carbon $N = 6$ in the molecules $Li_4(CH_3)_4$ and $CRu_6(CO)_{17}$ and in NaCl-type carbides. The amber-yellow(non-metallic) CaF_2-type Be_2 C is an interesting case. Not only is $N = 8$ for carbon, but one mole of beryllium carbide contains 6 moles of inner-shell 1s electrons and 8 moles of loosely bound electrons, to be compared with 16 moles required by the $2N$ paradigm.

There is another point where the two-digit Z values form their own category. The sodium atom and all subsequent atoms have the correlation energy (relative to the well-defined configuration optimized in the Hartree-Fock wave-function) greater than the first ionization energy, removing the back-bone of the variation principle. The undisputed utility of electron configurations [5] (also in trans-neon elements) ramifies to classificatory K-values in compounds [16]. Positive S values are also implicitly rendered unlikely by the Lewis paradigm, though $S = 5/2$ is particularly stable [11,31] in manganese (II) and iron (III), and $S = 7/2$ in europium (II), gadolinium (III) and terbium (IV) [7,33]. In more recent times, «ligand field» theory is frequently used in the reverse, number of electrons in the partly filled d-shell (and the S value) being evaluated from the observed absorption spectrum, assuming plausible N and symmetry.

The thesis defended [27] that N is mainly determined by relative atomic sizes can, obviously, not be the whole truth. When the amphoteric species in alkaline solution is $Be(OH_4^{-2}$ but $Pb(OH_3^-$ or when tetrahedral $TlCl_4^-$ is found in strong hydrochloric acid (where $[Co(NH_3)_6]$ $[TlCl_6]$ can be precipitated at once) other effects influence N. It might still be argued that $N = 3$ in BF_3 and NO_3^- because of the small central atom, but $N = 2$ must be enhanced by specific covalent bonding. Au(I), Hg(II) and Tl(III) show linear $N = 2$ like iodine (I) and xenon (II) in the isoelectronic series $BrAuBr^-$, BrHgBr; $NCAuCN^-$, NCHgCN; H_3CHgCH_3, $H_3CTlCH_3^+$, $H_3NAuNH_3^+$ and $H_3NHgNH_3^{+2}$.

Similar coordination can be due to steric hindrance as in $(H_3C)_3CBeC(CH_3)_3$ (when compared with $N = 4$ for beryllium in Be_2C) but it cannot be neglected that the CaF_2-type HgF_2 has $N = 8$. Earlier $K = 78$ have $N = 4$ in Os $(PF_3)_4^{-2}$ and $Ir(PF_3)_4^-$.

A further complication is that $N = 2$ may be bent rather than linear. It may be noted that the loss of Madelung stabilization [5] going from tetrahedral to quadratic $N = 4$ is quite marginal, though the latter symmetry (excepting stereochemical constraint from macrocyclic ligands) is concentrated on a few K-values, such als the p^2 systems bromine (III), iodine (III) and xenon (IV) and the diamagnetic d^8 systems. Contrary to linear CO_2, the monomeric species NO_2, NO_2^-,O_3,O_3^-,SO_2 and S_3^- (known to provide the blue colour [34] of lapis lazuli) are bent. This may have something to do with lone-pairs, but Lewis does not explain why O_3^- does not dimerize (as do neither O_2^+,O_2^- nor ClO_2). A tantalizing result [35] is that gaseous $CaCl_2$, $CaBr_2$, $SrBr_2$ and SrI_2 are linear (as one would expect from electrovalent bonding or almost any other hypothesis) but gaseous CaF_2, SrF_2, $SrCl_2$ and all four barium halides are bent. The armchair chemist may start talking about 4d and 5d orbitals being involved, but an alternative anti-climax is that when the ratio between the Goldschmidt ionic radii of the alkaline-earth cation and of the halide anion is above 0.648, the molecule is bent. But why?

The central hydrogen(I) in symmetric FHF^- was a pain in the neck for the $2N$ paradigm. However, hydride bridges [27,36] are quite fascinating too. Recently, the hydride bridge in $(OC)_5CrHCr(CO)_5^-$ was shown to be bent [37]. This chromium (0) complex is closely analogous to an iodide-bridged species. Diborane $H_2BH_2BH_2$ and $Zr(H_3BH)_4$ (having $N = 12$ like $U(H_3BH)_4$ syncrystallized [38] in the hafnium (IV) boranate) also show bent hydride bridges. On the other hand, the NaCl-type(non-metallic) hydrides LiH,NaH,KH,RbH and CsH have octahedral $N = 6$. The perovskites $BaLiH_3$ and $EuLiH_3$ also show $N = 6$ for hydride being bound to two Li(I) on one Cartesian axis and to four M(II) on the two other axes.

The paradigm of 2*N* electrons is farther away from universality than ever since 1916. As many unreliable explanations, it makes correct predictions in about a third of the cases. Actually, it is worthwhile to ask the opposite question: why does the paradigm work for alkanes, tetra(alkyl)ammonium ions, diamond, gallium arsenide and H_2? Is there a specific correspondance between the M.O. (of more general scope) and the basis set of (orthogonalized?) bond electron-pair functions in these cases without lone-pairs? Besides the rather collapsing hybridization theory, another off-spring of the Lewis paradigm is the Kimball model [39] of electron pairs confined in individual non-overlapping spheres. Also in this case, the importance of the kinetic energy operator [17] for chemical bonding has been underestimated. It seems that in 1916, the energetic difference between two electrons (or more strictly speaking, between their M.O.) in a given compound was not evident, though *Kossel* [14] certainly considered quantitative energy values derived from atomic spectra [5,40] and X-ray spectra, which in this situation were the percursors of photo-electron spectra.

There is a close connection between the theory of oxidizing character (i.e. the electron affinity in the chemical species) and the theory of acidic behaviour [36,41] though we should not overlook the (quite rare) cases of non-oxidizing strong anti-bases (Lewis acids) such as boron(III) and aluminium(III) serving as useful traffic signs and indicia. Though H_3O^+ can (reversibly at pH = 7) oxidize $Mn(CO)_5^-$ to the manganese(I) hydride complex $HMn(CO)_5$, and H_3O^+ violently oxidizes H^- to H_2, a single counter-example suffices to show that not all anti-bases are perceptibly oxidizing. There is, however, a weak doubt [5] whether $H_3BMn(CO)_5^-$ is a Mn(I) complex of a previously not recognized ligand BH_3^{-2} isoelectronic with CH_3^- and NH_3. On the other hand, it is an experimental fact [27] that aqua ions of Fe(III), Cu(II), Pd(II), Hg(II), Tl(III) and most extremely Au(III) are much stronger Brønsted acids than ions with the same z and similar radii.

The idea of *Lavoisier* that all acids contain oxygen, encountered multiple exceptions, and finally vanished. The paradigm of 2*N* electrons in *N* bonds is not in a much better shape.

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