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Breakdown of the Hybridization Theory and the Ligand Field Problem

By Christian Klixbüll Jørgensen
Département de Chimie Physique, Université de Genève, 1211 Geneva 4

Summary

Outside the narrow group of elements from beryllium to fluorine, the assumption of an approximately common radial function to be multiplied by a sum of angular functions belonging to different shells is not at all plausible. The apparent paradox in the behaviour of anti-bonding d-like orbitals in transition group complexes and the intensities of absorption bands (which are unexpectedly high in almost quadratic chromophores formed by copper [II] and palladium [II]) are discussed and compared with simpler diatomic molecules.

The Illusion of N Orbitals Needed for the Bonding of N Ligands

It is a sociological fact that a major part of contemporary chemists think in terms of hybridized orbitals. This is a unreasonable model for almost all compounds containing atoms with higher atomic number Z than 13, that of aluminium. It is obvious that the fair validity of the octet rule in boron, carbon and nitrogen compounds and the replacement of classical valences by electron pairs are the origin of this extrapolation to heavier elements. It turns out that one of the fundamental ideas behind the hybridization model of N equivalent orbitals in compounds having N ligating atoms bound to a central atom also is attractive in the very specific case of boron, carbon and nitrogen. In spherical symmetry[1-3], as occurring in atoms and isolated monatomic ions, the orbitals are one-electron functions being the product of an angular function A_l and a radial function R_{nl}. Whereas the radial function of given nl-shell can have rather different shapes dependent on the atomic number and the ionic charge, and a common characteristic is $(n-l-1)$ radial nodes, i.e. finite positive r values for which R_{nl} is zero, the angular function A_l is a much more invariant entity being the same linear combination of homogeneous polynomials $(x^a y^b z^c/r^l)$ in the Cartesian coordinates (where $a+b+c=l$ and a,b,c are non-negative integers) as in a one-electron atom such as H or He^+. Each shell has $(2l+1)$ mutually orthogonal angular functions, which can be written for the three first l-values:

$$\begin{aligned}
s\,(l=0)&:\quad 1,\\
p\,(l=1)&:\quad \sqrt{3}\,(x/r),\ \sqrt{3}\,(y/r),\ \sqrt{3}\,(z/r),\\
d\,(l=2)&:\quad \sqrt{15}\,(xy/r^2),\ \sqrt{15}\,(xz/r^2),\ \sqrt{15}\,(yz/r^2),\\
&\quad\ \ \sqrt{15}\,(x^2-y^2)/2r^2,\ \sqrt{5}\,(3z^2-r^2)/2r^2.
\end{aligned}$$

One might have expected six polynomials of second degree, but one of them has to be removed because $(x^2+y^2+z^2)/r^2$ is another way of writing the number 1. Actually, four of the five remaining d-functions have the same geometrical shape (like a quadrupole or a tetrafolium) and can be obtained by appropriate rotation of the Cartesian axes, either 45° in the xy-plane transforming (xy) into $(x^2-y^2)/2$, or by a cyclic permutation of the names x, y and z. The outsider, the fifth d-function, is proportional to $(3z^2-r^2) = (2z^2-x^2-y^2)$. As a matter of fact, any angular function $\sqrt{3}\,(ax+by+cz)/r$ normalized by the condition $(a^2+b^2+c^2) = 1$ has exactly the same shape as a conventional p-function, only oriented in a different direction. Pauling's hybridizations sp, sp^2 and sp^3 are all special cases of the general expression

$$A_P = [\sqrt{3}\,(ax+by+cz)/r] + d$$

with the normalization condition $a^2+b^2+c^2+d^2 = 1$. The important point is that in the $2p$ group (B,C,N,O, F,Ne) the radial functions R_{2s} and R_{2p} are rather similar (except that R_{2s} has a radial node for a low r-value in the middle of the $1s$-electronic density) and correspondingly, it is not a too bad approximation to put a common radial function R_P outside parenthesis, considering the hybridized one-electron function $A_P R_P$ [having the electronic density $(A_P)^2(R_P)^2$]. The physical origin of this possibility of a common radial function R_P is that the $2p$ group has only two electrons in the atomic core ($1s$ with a very small average radius). In heavier elements, the large number of electrons in the atomic core modifies R_{nl} with the same n to a great extent. It is, of course, always possible to discuss linear combinations $aA_{3s}R_{3s}+bA_{3p}R_{3p}$ but it is not feasible to put a common radial function outside parenthesis. This is particularly true for the iron group complexes where R_{3d}, R_{4s} and R_{4p} are entirely different. Actually, their average radii $\langle r\rangle$ have ratios close to 1:3:4, which is a much more important difference than the zero, three and two radial nodes.

[1] C. K. Jørgensen, *Orbitals in Atoms and Molecules*, Academic Press, London 1962.
[2] C. K. Jørgensen, *Oxidation Numbers and Oxidation States*, Verlag Springer, Berlin 1969.
[3] C. K. Jørgensen, *Modern Aspects of Ligand Field Theory*, North-Holland Publishing Co., Amsterdam 1971.

We return below to the discrepancy between an even approximate validity of d^2sp^3 in octahedral complexes, suggesting coinciding parity-allowed and parity-forbidden transitions, and the absorption spectra observed [with possible rare exceptions such as $Cr(CO)_6$ and $Ir(CN)_6^{-3}$]. A much more direct difficulty in groundstates is that $2p$ group elements simply have no more than four orbitals available for chemical bonding, whereas their coordination number N can be 5, 6 or 8. For instance, the isoelectronic compounds CsF, BaO, LaN and isoelectronic LuN and HfC all cristallize in the NaCl type where both atoms have $N = 6$, and it cannot be argued that they are fully ionic in direction of N(−III) and C(−IV). This argument is not fundamentally altered by the fact that the three latter compounds are metallic (though LaN and LuN probably are because of a small deviation from stoichiometry). The series of compounds BaS, BaTe, green MnS, CoO, NiO and CdO all cristallize in NaCl type, and it cannot be argued that they are fully ionic though oxide has only the three $2p$ orbitals and the (much stabler) $2s$ orbital to take care of covalent bonding. In organo-metallic compounds of small atoms such as lithium and beryllium, N for carbon is frequently[4] 5, 6 or 8. This is particularly true for the colourless Be_2C cristallizing in fluorite type though it cannot seriously be considered as fully ionic, consisting of Be^{+2} and C^{-4}. KREBS[5] suggested the idea of mesomery in such cases, four orbitals of carbon taking care of eight strictly equivalent bonds. This explanation is not very attractive, though it can explain almost everything, because it would immediately be exploited by photo-electron spectroscopists suggesting that tetrahedral carbon uses mesomeric permutations of the three $2p$ orbitals having about half the ionization energy of the $2s$ orbital both in the carbon atom and in compounds such as methane.

The Non-bonding Orbitals and a Simple Model of the Ligand Field Problem

The hybridization model applied to iron group complexes considers nine orbitals of the central atom M. Dependent on the symmetry of the chromophore MX_N, some (normally 9-N, with exception of the quadratic chromophores) of the $3d$ orbitals being non-bonding, and the others (including $4s$ and the three $4p$) are σ-bonding, $2N$ electrons donated from the N ligating atoms (which may occur in bidentate or multidentate ligands) occupying the bonding orbitals. This corresponds to the idea of "effective atomic number" (so dear to metallo-organic chemists) going back to SIDGWICK. Quadratic MX_4 has only four non-bonding $3d$ orbitals, the bonding is taken care of by one $3d(x^2-y^2)/r^2$, the $4s$ and two $4p(x/r)$ and (y/r). A minor variation is that certain tetrahedral chromophores in the beginning of the transition groups according to KIMBALL are said to have d^3s rather than sp^3 hybridization.

When only the groundstates are considered, there is no major difference between the predictions of the M.O. (molecular orbital) theory described below and the hybridization theory, when the non-bonding d orbitals are not completely filled. Thus, all octahedral chromium (III) complexes have three electrons with parallel spins in these three orbitals, whereas $Fe(CN)_6^{-3}$ and $IrCl_6^{-2}$ have five electrons in such a sub-shell consisting of three orbitals with necessarily the same energy in cubic symmetries having equivalent Cartesian axes (since the non-bonding orbitals have angular functions proportional to xy, xz and yz, obtained by cyclic permutation). The difficulties for groundstates start when additional d electrons have to be added besides the filled non-bonding orbitals. Thus, octahedral nickel(II) chromophores such as $Ni(II)O_6$ known from the hexa-aqua ion and many mixed oxides ($NiTiO_3$, $Ni_xMg_{1-x}O$) and glasses and $Ni(II)N_6$ known from $Ni(NH_3)_6^{+2}$ and many amine complexes all have two electrons too much, which in M.O. theory are situated to the first approximation (and having parallel spin) in the higher sub-shell consisting of the two $3d$-orbitals having angular functions proportional to (x^2-y^2) and $(3z^2-r^2)$, and six electrons in the lower sub-shell. As a matter of fact, the spectroscopic oxidation states[2,6] are defined from the preponderant electron configuration of the groundstate; eight d-like electrons correspond to nickel(II) whereas d^7 is Ni(III) and d^6 *ipso facto* is Ni(IV). The hybridization theory ascribes the two additional electrons to higher orbitals, such as $4d$. It was believed some time ago that one diamagnetic octahedral nickel(II) complex exists with three bidentate diarsine ligands, and the theorists wrote long papers suggesting that the two additional electrons are situated in the $5s$ orbital. However, this complex suffers the small ontological imperfection that it does not exist; under the preparation, a tridentate arsine is formed[7] and the chromophore is square-pyramidal $Ni(II)As_5$. Anyhow, the hybridization model suggests that octahedral Ni(II) is readily oxidized to Ni(IV) in blatant disagreement with experience. The situation is even more serious in quadratic $Cu(II)X_4$. Here, one additional electron has to find its niche, and in many text-books, it is accommodated in the $4p(z/r)$ orbital perpendicular on the molecular plane. However, electron spin resonance of copper (II) complexes[8] showed that the unpaired electron is in the $3d(x^2-y^2)/r^2$ orbital having maximum density at the positions of the four ligands on the x- and y-axes. One way out of this difficulty is to suggest that all known copper(II) complexes

[4] C.K. JØRGENSEN, *Structure & Bonding 6* (1969) 94.
[5] H. KREBS, *Grundzüge der Anorganischen Kristallchemie*, Verlag Enke, Stuttgart 1968.
[6] C.K. JØRGENSEN, *Chimia 23* (1969) 292.
[7] B. BOSNICH, R.S. NYHOLM, P.J. PAULING and M.L. TOBE, *J. Amer. Chem. Soc. 90* (1968) 4741.
[8] R.L. BELFORD, M. CALVIN and G. BELFORD, *J. Chem. Physics 26* (1957) 1165.

are ionic in PAULING's sense, being essentially $3d^9$ systems perturbed by negatively charged ligating atoms. This is not particularly palatable, because Cu(II) definitely is the most covalent case among the various M(II) in the $3d$ group, and not dramatically different from Cr(III) and Co(III) except for the rapid kinetics. It cannot even be argued that slow reactions always indicate strong covalent bonding; $Hg(CN)_2$ and *fac*-$Pt(CH_3)_3(H_2O)_3^+$ exchange cyanide and aqua[9] ligands rapidly. Since 1956, it is generally agreed that the M.O. theory in the specific version called ligand field theory[3] is far more appropriate[10,11] than hybridization theory to describe both groundstates and excited states of transition-group complexes. The hybridization model is notoriously unable to handle the excited states[12] because the absorption bands in the visible of all kinds of complexes [e.g. octahedral chromium(III) and cobalt (III)] are due to transitions of one electron from the non-bonding sub-shell to one of the anti-bonding orbitals accommodating two electrons in $Ni(II)X_6$ and one in Cu(II).

Nevertheless, a psychological problem remains for the chemist: *primo* that the anti-bonding d-like orbitals exist though PAULING does not speak about them, and *secundo* that they show anomalous behaviour in the sense that they are attracted by the atom having the *lowest* electronegativity. Thus, the least covalent compounds formed by the ligands of high electronegativity, such as fluoride, and central atoms which are only weakly oxidizing, such as Mn(II) and Ni(II), have the anti-bonding orbital almost exclusively concentrated on the central atom and the bonding orbital centered on the ligand. This behaviour is induced by the necessity of the two M.O. to remain orthogonal[3]. On the other hand, ligands of lower electronegativity, such as bromide or sulphur-containing ligands[13], and strongly oxidizing central atoms, such as Mn(IV), Ni(IV) or Pt(IV), induce a more balanced distribution of electronic density, the anti-bonding orbital being somewhat more on the central atom than on the ligands whereas it is the other way round for the bonding orbital. We call this tendency the *ligand field problem.*

A simple example helping to understand the ligand field problem is the M.O. formed by linear combination of atomic orbitals (L.C.A.O.) of the $1s$ orbitals of two very light atoms such as hydrogen or helium. In homonuclear diatomic molecules, the density (the square of the one-electron function) is necessarily the same on each atom. On Fig. 1, it is seen that H_2^+ has one and H_2 two electrons in the bonding combination having no

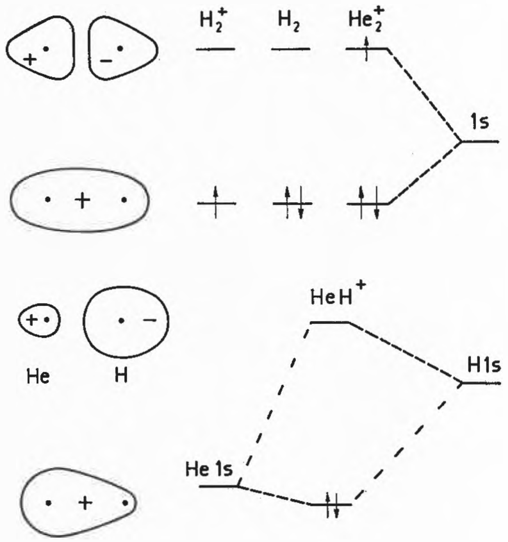

Fig. 1. The anti-bonding and bonding M.O. in simple diatomic species. In the heteronuclear case, the upper, anti-bonding orbital consists mainly of the atomic orbital of the least electronegative atom (here hydrogen $1s$) whereas the opposite is true for the lower, bonding orbital. The plus and minus signs only indicate the relative phase of each region of the wave-function (which is not essentially changed by a multiplication with -1; the square of the one-electron function indicates the distribution of electronic density)

node-plane between the two nuclei. This would also be true for He_2^{+2} but because of the electrostatic repulsion between the two dissociation products He^+, this molecular ion is not stable in the gaseous state. In solvents of high dielectric constants and in crystals, it is possible[6] to stabilize species with two positive charges, such as Hg_2^{+2}. On the other hand, He_2^+ has two electrons in the bonding and one electron in the anti-bonding orbital having a node-plane between the two nuclei. This species is perfectly stable in the gaseous state toward dissociation in He and He^+ though it is far too oxidizing to be isolated in salts, even BeF_4^{-2} or BF_4^- supplying a strong MADELUNG potential would still evolve F_2. The molecule He_2 containing two electrons both in the bonding and the anti-bonding orbitals dissociates spontaneously to atoms in the gaseous state. Quite generally, the anti-bonding M.O. are 1.5 to 3 times more anti-bonding than the bonding M.O. are bonding. This repulsion between closed shells explains why compounds do not implode. In a purely electrostatic description of an ionic salt, the bonding energy relative to gaseous ions would be inversely proportional with the linear extension of the unit cell. However, the core-repulsion prevents this implosion at a definite value of the internuclear distances. An apparent exception to this rule exists in the diatomic molecule BH isoelectronic with BeHe, but a closer analysis[3] shows that it contains a bonding and a non-bonding (rear-side lone-pair) combination filled among three M.O. formed by H $1s$, B $2s$ and B $2p(z/r)$.

When the diatomic molecule is heteronuclear, the bonding M.O. is deformed in such a way as to have higher density on the atom with highest electronega-

[9] D.E. CLEGG, J.R. HALL and N.S. HAM, *Austral. J. Chem. 23* (1970) 1981.
[10] L.E. ORGEL, *Introduction to Transition-Metal Chemistry*, Methuen, London 1960 (2. Ed. 1966).
[11] W. SCHNEIDER, *Einführung in die Koordinationschemie*, Verlag Springer, Berlin 1968.
[12] C.K. JØRGENSEN, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford 1962.
[13] C.K. JØRGENSEN, *Inorg. Chim. Acta Reviews (Padova) 2* (1968) 65.

tivity. In order to remain orthogonal on the bonding M.O., the anti-bonding orbital not only has a nodal surface between the two nuclei, but also a higher density on the *least* electronegative atom. On Fig. 1, this tendency is exemplified by HeH^+. The groundstate contains two electrons in the bonding orbital, and hence, the fractional charge on helium is less positive than on hydrogen. The excited state having one electron in each orbital corresponds to an electron transfer band where hydrogen (I) $(1s^0)$ is reduced to hydrogen (0) $(1s^1)$ much in the same way as electron transfer to empty $3d$-orbitals gives the yellow colour of CrO_4^{-2} and purple colour of MnO_4^-. The chemical reason why HeH^+ cannot be isolated is that it is a too strong acid for avoiding proton transfer to all known solvents. There is some hope that the corresponding species KrH^+ and XeH^+ might be prepared in solvents which are very weak BRØNSTED bases; the protonated noble gases are quite stable against dissociation.

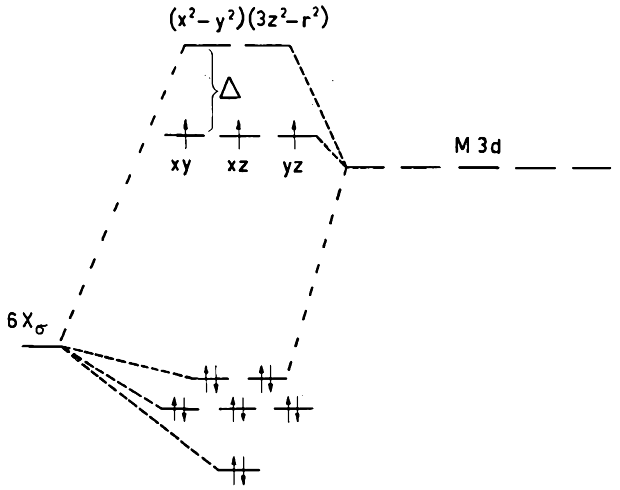

Fig. 2. The five *d*-like orbitals (characterized by their angular dependence) and the six bonding orbitals of an octahedral chromophore MX_6 where the ligands X have each only one lone-pair. The X nuclei are situated on the Cartesian axes at equal distance from the M nucleus at origo. The distribution of electrons shown as arrows correspond to a d^3 system [such as chromium (III) or manganese (IV)] having one electron in each of the three orbitals constituting the lower sub-shell. These three orbitals are, to the first approximation, non-bonding and localized on the central atom M

The main difference between HeH^+ and the *d*-group complexes is the non-bonding *d*-electrons. Fig. 2 shows the important orbitals of an octahedral chromophore MX_6 where the ligands X have only one lone-pair (like H^- and NH_3). If the ligands have three orbitals in a closed *p*-shell (such as O^{-2}, F^-, Cl^-, Br^-, I^-) a set of twelve π-orbitals occur above the six σ-orbitals producing an interesting and complicated structure of the electron transfer bands[14, 15]. For our purposes, the important point is that PAULING's hybrids are formed from the six *bonding* orbitals (mainly concentrated on X) and then, the non-bonding orbitals (here a sub-shell of three degenerate orbitals) are recognized. However, nobody maintains seriously today that cobalt (III) is a d^{10} system having the corresponding two (among the six) σ-bonding orbitals and the sub-shell filled. Rather, it is a d^6 system because the five *d*-like orbitals on Fig. 2 are the latter sub-shell *and* the two anti-bonding orbitals. Nickel (II) is a d^8 system *because* the two anti-bonding orbitals contain each an electron. The virtue of the ligand field description is that it displaced the attention from the manifold of the bonding and the non-bonding orbitals to the five really *d*-like orbitals constituting the non-bonding and the anti-bonding sub-shells. The energy difference Δ between the two sub-shells in octahedral MX_6 (also called $10\,Dq$ in literature) on Fig. 2 has the same origin as any difference in anti-bonding character of other M.O. and it cannot be considered[12] as the result of the electrostatic perturbation of the non-spherical (small) part of the MADELUNG potential. It is probable[3, 16] that the main contribution to sub-shell energy differences is the increased local contribution to the kinetic energy in the bond region where the new node-plane of Fig. 1 occurs.

Absorption Spectra and Mixing of *l*-Values in Complexes

The absorption bands in the visible and near ultraviolet are due to transitions which, to the first approximation, can be classified in five categories:

1. *Transitions involving almost degenerate orbitals.* Such absorption bands are narrow and correspond to transitions not modifying the total electronic density in our three-dimensional space. This is particularly true for internal transitions in the configurations $4f^q$ and $5f^q$ producing spectra similar to those of gaseous ions in spherical symmetry. The minor energy differences between the seven *f* orbitals can be explained by the *angular overlap model*[17, 18] which has been generalized to *d*-group chromophores too[3, 19]. The spin-forbidden transitions in *d*-group compounds involving the same, partly filled, sub-shell also belong to this category, producing narrow (and sometimes luminescent) absorption bands.
2. *Transitions from one sub-shell to another.* These correspond to the broad and moderately weak absorption bands studied by ligand field theory applied to the *d*-groups. Incidentally, most such bands correspond to a jump of one electron from a lower to a higher sub-shell to a good approximation, with exception of high-spin manganese (II) and iron (III) complexes

[14] C. K. JØRGENSEN, *Halogen Chemistry 1* (1967) 265, Academic Press, London.
[15] C. K. JØRGENSEN, *Progr. Inorg. Chem. 12* (1970) 101.
[16] C. K. JØRGENSEN, *Chem. Physic. Letters 1* (1967) 11.
[17] C. K. JØRGENSEN, R. PAPPALARDO and H. H. SCHMIDTKE, *J. Chem. Physics 39* (1962) 1422.
[18] D. KUSE and C. K. JØRGENSEN, *Chem. Physic. Letters 1* (1967) 314.
[19] C. E. SCHÄFFER, *Proceed. 12. ICCC (Sydney, 1969)*, Butterworth, London 1971.

where the two first absorption bands correspond to a jump in the opposite direction (but since $S = 5/2$ of the groundstate is changed to $S = 3/2$, the concomitant defavourable increase of interelectronic repulsion makes the groundstate the most stable with one electron in each of the five *d*-like orbitals) and with exception of two of the spin-allowed transitions of tetrahedral cobalt (II) and octahedral vanadium (II) and nickel (II) which are mixtures of about equal amounts of one- and two-electron jumps.

3. *Inter-shell transitions.* The electron remains roughly localized on the central atom, but jumps from one nl-shell to another. In gaseous molecules, such excited states are called RYDBERG states. Characteristic examples are $4f \rightarrow 5d$ transitions in lanthanides, $5f \rightarrow 6d$ transitions in Pa (IV), U (III), U (IV) and *trans*-uranium compounds[2] and $5p \rightarrow 6s$ and $5p \rightarrow 5d$ transitions in iodide and the isoelectronic xenon atom[14]. In post-transition group complexes, $5s \rightarrow 5p$ seem to occur in Sn (II), Sb (III) and Te (IV), and $6s \rightarrow 6p$ in Tl (I), Pb (II) and Bi (III). However, the effect of *l*-mixing to be discussed below may make such a description slightly artificial.
4. *Normal electron transfer bands* go from M.O. mainly localized on reducing ligand to empty or partly filled *d*- of *f*-orbitals of the central atom, or in rarer cases from next-neighbour atoms of metallic elements, such as $4d$ of Ag (I) or $6s$ of Tl (I) to such an empty or partly filled *d*- or *f*-shell[15]. The oxidation number[2] of the central atom is decreased by one unit in the excited state; the ligands may collectively loose an electron and are no longer in a closed-shell situation. Most strong colours used in colorimetric reactions and in pigments are due to such transitions.
5. *Inverted electron transfer bands* go from a partly filled or fully occupied [say, copper (I)] *d*-shell to low-lying, empty M.O. In actual practice, such transitions are only perceptible in the case of conjugated organic ligands such as dipyridyl, phenanthroline, acetylacetonate, picolinate etc. It may be difficult to make a sharp distinction from inter-shell transitions, e.g. when iodide occurs close to such conjugated systems.

For our purposes, it is not without interest to note that $Fe(H_2O)_6^{+2}$ and other reducing aqua ions have a weak, broad absorption band in the ultra-violet caused by $3d \rightarrow 4s$ transitions with a certain similarity with category 5. Actually, this puts a lower limit to the energy of the anti-bonding component of $4s$-character, making it energetically quite separate from $3d$, as would already be true for the radial extension.

Obviously, there is a quite legitimate use of hybridization in M.O. theory, though it is recommended to call it mixing of *l*-values. For instance, BH, CO and N_2 contain lone-pairs having mixed $2s$ and $2p(z/r)$ character if *z* is the linear axis of the diatomic molecule. Usually, the effects of chemical bonding are weaker than the energy differences between nl-shells of importance for the chemical bonding, and the *l*-mixing is not very large. But it can have spectacular effects on the preferred stereochemistry[20] and for instance, $PtCl_4^{-2}$ is known[21] to have the orbital $5d(3z^2 - r^2)$ perpendicular on the molecular plane being depleted in the equatorial plane by a positive admixture of $6s$-character, leaving this $5d^8$ system with four almost non-bonding orbitals and the empty $5d(x^2 - y^2)$ strongly anti-bonding. The opposite mixture takes place[22] in linear Cu (I), Ag (I), Au (I) and Hg (II) complexes where the spherically symmetric d^{10} electronic density is depleted along the *z*-axis, decreasing the total amount of anti-bonding.

The most important effect of small deviations on an instantaneous picture from a high symmetry (where the point-group includes a center of inversion) is that the parity-forbidden inter-sub-shell transitions obtain intensity by mixing with excited states of opposite parity, mainly belonging to electron transfer bands[12, 23]. However, copper (II) amine complexes have unexpectedly high absorption band intensities[24, 25], and it can be argued that the preferred stereochemistry is square-pyramidal even in the dark blue $Cu(NH_3)_4(H_2O)^{+2}$ [anhydrous $Cu(NH_3)_4^{+2}$ is pink[26]]. Similar complications are known from palladium (II) complexes[27, 28] which seem to have an intrinsic tendency toward two short and two long bonds in an approximate *cis*-quadratic arrangement. These cases[29] seem to have *l*-mixing like the post-transition group approximate s^2 systems. Actually, ligand field arguments are as applicable to *p*-group complexes[14] and some, such as linear ICl_2^- and XeF_2 or quadratic BrF_4^-, ICl_4^- and XeF_4 conserve their center of inversion, whereas the pyramidal NH_3, SO_3^{-2}, ClO_3^-, $SnCl_3^-$, $SbCl_3$, $TeCl_3^+$, IO_3^- and XeO_3 must have strong mixing of *s*- and *p*-character in the lone-pair.

One of the alleged advantages of the hybridization theory is its ability to predict the most stable stereochemistry of a given chromophore. This is to a large extent a circular explanation[3, 20] but one has to admit that M.O. theory is not very suitable, at the same time, to find the most favourable internuclear distances (sufficient to describe the molecular symmetry except for optical activity) and the relative M.O. energies. As a matter of fact, the angular dependence of chemical bonding energy is very weak, as seen from the existence of cyclopropane and from the very small energy needed to

[20] C.K.JØRGENSEN, *Chem. Physic. Letters 3* (1969) 380.
[21] F.A.COTTON and C.B.HARRIS, *Inorg. Chem. 6* (1967) 369.
[22] C.K.JØRGENSEN and J.POURADIER, *J. Chim. Physique 67* (1970) 124.
[23] R.F.FENSKE, *J. Amer. Chem. Soc. 89* (1967) 252.
[24] C.K.JØRGENSEN, *Advances Chem. Physics 5* (1963) 33.
[25] V.ROMANO and J.BJERRUM, *Acta Chem. Scand. 24* (1970) 1551.
[26] W.SCHNEIDER and P.BACCINI, *Helv. Chim. Acta 52* (1969) 1955.
[27] L.RASMUSSEN and C.K.JØRGENSEN, *Acta Chem. Scand. 22* (1968) 2313.
[28] L.RASMUSSEN and C.K.JØRGENSEN, *Inorg. Chim. Acta (Padova) 3* (1969) 543 and 547.
[29] H.H.SCHMIDTKE and C.K.JØRGENSEN, *Chem. Physic. Letters 5* (1970) 202.

make ammonia planar rather than pyramidal. The whole question of discrepancies between molecular symmetries at different time-scales and at time-average (such as a crystal structure) and of instantaneous symmetry derived from visible spectra or photo-electron processes is very intricate[3].

Whereas the electrostatic model of the ligand field collapsed a definite day in April 1956, it is more difficult to say when the hybridization theory was finally discredited by the study of absorption spectra[30,31] though it was distinctly happening before 1955.

Active Life of Secondary School Teachers

It is well-known from the history of sciences that theories sometimes are scrapped completely and irreversibly. However, we are accustomed to this process taking several generations, such as was true for the geocentric and the heliocentric model of the motion of the planets. In this century, such an evolution may take only two or five years. In the specific case of the hybridization theory, it is essentially kept alive by teachers in secondary schools (Mittelschulen) and propaedeutic courses at some universities. The main difficulty is that such teachers carry on for about 40 years with the result that today's teaching reflect the position of chemistry and physics between 1920 and 1960. Since, in a civilized country, people should not be killed, the alternative solution is refresher courses during extended holidays of the students. However, material such as the hybridization theory tends to be considered a valuable treasure, and as described in two recent best-sellers[32,33] it can even serve the rather undesirable purpose of a Darwinian selection of mediocrity. Theories do not become respectable just because they were believed to some extent between 1931 and 1954, except as examples to be studied in the history of sciences. The related description of "resonance between ionic and covalent structures" has been treated elsewhere[12]; in molecules containing more than four electrons, the difficulties are even worse. The positive aspect of this situation is that suitably chosen orbitals are capable of classifying low energy levels of both monatomic and polyatomic entities.

[30] H. HARTMANN and H. L. SCHLÄFER, *Z. Naturforsch.* *6a* (1951) 754 and 760.

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