Forschung Wissenschaft

The Third Revolution in "Ligand Field" Theory—the Ionization Energy of the Partly Filled Shell is Sometimes Larger than of the Ligand Orbitals

By CHRISTIAN KLIXBÜLL JØRGENSEN
Département de Chimie Physique, Université de Genève, 1211 Geneva 4

Summary

In several *d*-group and in most 4*f* group compounds, the ionization energy of the partly filled shell has been shown by photoelectron spectrometry to be higher than of the loosest bound filled molecular orbitals. This has the unexpected consequence that the anti-bonding M.O. has higher ionization energy than the corresponding bonding M.O. of the same symmetry type, and invites thinking about what are sub-shell energy differences in "ligand field" theory.

The interatomic COULOMB potential (in the following called the MADELUNG potential, not only in crystals, but also in small molecules) in a given point $V_{\mathrm{Mad}}(x, y, z)$ is the sum of the electric charges q_i divided by their distance R_i from the point considered. It is a consequence of classical electrostatic theory that V_{Mad} in a sphere not containing any of the charges can be written as the sum of components having the same angular dependence as the $(2l+1)$ different A_l for orbitals in spherical symmetry multiplied by radial functions (proportional to r^l/R^{l+1} if the charges considered as sources of the electric field all have the distance R from the center of the sphere). In particular, the spherically symmetric component $V_0(r)$ is constant inside the sphere and simply the sum over q_i/R. This is the reason why the MADELUNG energy of crystals containing closed-shell cations and anions (isoelectronic with the noble gases) or other spherically symmetric cations (such as the half-filled shells d^5 or f^7) can be calculated as if all the charges were points. The validity of this approximation is not based on the absence of A_l components with positive l but on the fact that they have vanishing first-order perturbation energy when acting on electronic densities possessing spherical symmetry. We call the (rather small) difference

$$V_{\mathrm{Bethe}}(x,y,z) = V_{\mathrm{Mad}}(x,y,z) - V_0(r) \qquad (1)$$

in view of the suggestion by BETHE[1] that the energy differences between the five *d*-orbitals or between the seven *f*-orbitals in transition-group compounds are due to perturbations by the potential (1). This hypothesis was called crystal field theory, but when the emphasis shifted toward oligo-atomic chromophores containing a central atom M surrounded by a small number N of first-neighbour atoms X, the name changed to "ligand field theory". Some authors define the latter concept by reference to the partly delocalized M.O. (molecular orbitals) mentioned below, but then, the word "field" is a metaphore insinuating the change of the HARTREE potential not only consisting of adding the MADELUNG potential to the central field $U(r)$ of the gaseous ion M^{+z} having z equal to the oxidation number in the compound. Anyhow, the original electrostatic model was mainly used in magnetochemical discussions and got only applied to visible spectra of the octahedral chromophore $\mathrm{Cr(III)O_6}$ in ruby[2] and a few complexes in solution, such as the hexaqua ions of titanium(III), vanadium(III) and chromium(III)[3]. It has remained the subject of many books describing iron group[4] and lanthanide[5] spectra.

The first revolution is related to the diagrams of TANABE and SUGANO[6] showing the energy levels of a given number of *d*-electrons in an octahedral chromophore $\mathrm{MX_6}$ as a function of the sub-shell energy difference $\triangle$ (called 10 Dq in ancient literature) *divided* by a parameter of interelectronic repulsion, such as B introduced by RACAH. SCHÄFFER proposes to call the ratio $(\triangle/B)$ the ligand field strength Σ. The nephelauxetic (cloud-expanding) effect[7,8] is a decrease of the parameters of interelectronic repulsion compared with the corresponding gaseous ion, indicating an expansion of the partly filled shell. The spectroscopic consequences of the nephelauxetic effect had been observed[9,10] much earlier in lanthanide compounds (containing from two to twelve

---

[1] H. BETHE, *Ann. Physik 3* (1929) 133.
[2] R. FINKELSTEIN and J. H. VAN VLECK, *J. Chem. Physics 8* (1940) 790.
[3] H. HARTMANN and H. L. SCHLÄFER, *Z. Naturforsch. 6a* (1951) 754 and 760.
[4] H. L. SCHLÄFER and G. GLIEMANN, *Einführung in die Ligandenfeldtheorie*, Akademische Verlagsgesellschaft, Frankfurt am Main 1967.
[5] B. G. WYBOURNE, *Spectroscopic Properties of Rare Earths*, Interscience, New York 1965.
[6] Y. TANABE and S. SUGANO, *J. Physic. Soc. Japan 9* (1954) 753 and 766.
[7] C. E. SCHÄFFER and C. K. JØRGENSEN, *J. Inorg. Nucl. Chem. 8* (1958) 143.
[8] C. K. JØRGENSEN, *Progr. Inorg. Chem. 4* (1962) 73.
[9] K. A. HOFMANN and H. KIRMREUTHER, *Z. physik. Chem. 71* (1910) 312.
[10] F. EPHRAIM and R. BLOCH, *Ber. dtsch. Ges. 59* (1926) 2692 and *61* (1928) 65 and 72.

$4f$ electrons) shifting their narrow absorption bands slightly toward lower wave-numbers when the ligating atoms X have lower electronegativity (promoting covalent bonding) or unusually short distance R (as in oxides). The simplest model[11] compatible with this decreased interelectronic repulsion is the *expanded radial function* adapting to a new central field $U(r)$ changed by the invading electronic density arriving from the ligands.

However, it was realized almost at the same time that the partly filled shell is also modified by symmetry-restricted covalency forming anti-bonding M.O. with a nodal surface between M and X. In the LCAO approximation, the coefficient a to the M orbital produces an electronic density on the central atom proportional to a^2 and parameters of interelectronic repulsion approximately a^4 times the value for the expanded radial function. It is possible to estimate fractional atomic charges[12, 13] of the central atom taking into account both the central-field and symmetry-restricted covalency. Strictly speaking[14, 15] one would expect ten parameters of interelectronic repulsion in an octahedral d^q system, but in actual practice, it suffices to consider the more extensive delocalization of the upper σ-anti-bonding sub-shell than of the lower sub-shell which is non-bonding in ammonia complexes and otherwise at most π-anti-bonding. Curiously enough, the first clear-cut evidence for delocalization of the partly filled shell on the ligating atoms was the measurement[16] of the nuclear hyper-fine structure of the electron paramagnetic resonance spectrum of $IrCl_6^{-2}$ indicating $a^2 = 0.75$ for the lower sub-shell containing five $5d$-like electrons. It has been discussed in this journal[17] why it is a conceptual difficulty that the partly filled shell (being an anti-bonding M.O.) has its electronic density attracted by the atom having the *lowest* electronegativity (here M rather than X) and to the largest extent when M is not particularly oxidizing [such as manganese(II) or nickel(II)] and X not particularly reducing (such as F^- or H_2O). The opposite situation involving *e.g.* Mn(IV), Ni(IV), I^- and sulphur-containing ligands[18] corresponds to a more equal distribution of electronic density with a^2 close to a-half.

$\triangle$ can be discussed as an entirely phenomenological parameter (varying with the ligands and with the central atom in the spectrochemical series[13, 19]) but this approach is not satisfactory in the tetragonal chromophores having three independent sub-shell energy differences in the partly filled d-shell, nor in the lower symmetries having $2l$ independent sub-shell energy differences. The second revolution in "ligand field" theory was the introduction of the *angular overlap model* originally[20] intended to rationalize the (relatively small) orbital energy differences in $4f$ group compounds. The hypothesis that the anti-bonding orbitals have an energy increase proportional to the square of the overlap integral between the original M and X orbitals can be shown[21, 22] to be equiconsequential with a singular repulsive potential acting on the A_l orbitals of M at the positions of the ligand nuclei. The beauty of the angular overlap model is that the σ (or π) anti-bonding parameters can be transferred from one chromophore to another with different symmetry or differing coordination number N assuming invariant internuclear distance R. There is every reason to believe a rapid decrease of these parameters[23] with increasing R much in the same way as the dependence of $\triangle$ on R^{-5} in the old electrostatic model. Another result which has been generalized in the angular overlap model is the ratio $(-4/9)$ between $\triangle$ values in corresponding tetrahedral and octahedral chromophores. This treatment has been applied to substituted[24] and optically active[25] octahedral complexes, and the mathematical analysis further refined[26-28]. It is probable[29] that the physical origin of the σ-anti-bonding parameters is increased local contributions to the kinetic energy in the bond region between M and X, as RUEDENBERG[30] pointed out in a general discussion of anti-bonding M.O.

Though the evaluation of interelectronic repulsion in different energy levels of the partly filled l-shell remains a distinctive feature of "ligand field" theory[29] it is obvious that there is no sharp frontier with the general M.O. treatment of heteronuclear molecules and polyatomic ions. HÜCKEL considered homo-atomic planar systems having identical diagonal elements of energy of all the orbitals. If only one kind of nearest-neighbour interactions occur, they can be described by a single non-diagonal element frequently called β. In this case, the eigen-values differ by (fractional) multiples of β and the problem is exclusively topological. When different atoms occur in a conjugated planar molecule, such as pyridine, it is customary to write the difference between the diagonal elements α_N and α_C as a constant times β. The extension of this model to transition-group complexes with α_X much more negative than α_M produces σ-anti-bonding parameters of the angular overlap model $\beta^2/(\alpha_M - \alpha_X)$. WOLFSBERG and HELMHOLZ suggested β to be the product of the overlap integral S_{MX} and an appropriate function involving the average of α_M and α_X. This model was quite popular[31, 32] around 1962. If β is related to the kinetic energy operator in the bond region[29] the dependence on α_M and α_X is more indirect. Anyhow, these models have the undoubted advantage that the anti-bonding M.O. has its energy increased to a higher extent than the bonding M.O. is stabilized. The repulsion between atomic cores preventing the implosion inherent in all electrostatic models (where a stable system becomes 10 times more stable by being 10 times smaller) which was introduced in the description of ionic crystals by BORN corresponds to this overall destabilization by filling both the anti-bonding and the bonding M.O. However, it is imperative[33] to take the influence of the MADELUNG potential on α_M and α_X into account. Actually, in sufficiently heteropolar molecules, it is a better approximation to neglect the covalent bonding and estimate the total energy from differential ionization energies[13, 33] superposed the MADELUNG potential from fractional atomic charges than to make the opposite approximation as originally done in the model proposed by Wolfsberg and Helmholz.

The oxidation state of the central atom in a transition-group compound is defined[13] from the number of *d*- or *f*-like electrons in the partly filled shell. It would perhaps be expected that a given oxidation state would only be stable if the ionization energy I_M of the partly filled shell is lower than I_X of the loosest bound, filled M.O. on the ligands. However, a more correct opinion is that the *electron affinity* A_M of the partly filled shell is necessarily smaller than I_X. It had already been suggested[32] that a combination of a sufficiently oxidizing central atom and sufficiently reducing ligands (such as $CuBr_4^{-2}$ or OsI_6^{-2}) may have I_M above I_X. The third revolution happening to "ligand field" theory in 1971 is that this is the case for several *d*-group and almost every 4*f* group compound. It must be said in all fairness that this had been foreseen by certain M.O. theorists[34] but this particular result was somewhat swamped by the unfavourable noise-to-signal ratio in M.O. calculations. The two main difficulties are the deviations from Koopmans behaviour discussed below, and the occurrence of unrealistic, and frequently positive, one-electron energies in complex anions. The latter mistake can be remedied by the introduction of a constant attractive Madelung potential representing the surrounding cations in solid compounds or the hydration energy (of a perfect dielectric solvent) corresponds to a potential equal to the charge of the anion divided by twice its radius.

Before the measurements of photo-electron spectra of solid transition-group compounds, the major type of experimental evidence to be compared with calculations of orbital energies was visible and ultra-violet spectra, and in particular *electron transfer spectra*[35] where the excited state has the central atom containing an electron more in a *s*-, *d*- or *f*-like shell than in the groundstate, whereas the ligands are collectively oxidized[13] having lost an electron from a delocalized M.O. It is perfectly true[32] that these excitation energies are not exactly the difference between the ionization energies I_X and I_M but, to the first approximation,

$$I_X - I_M + J(\mathrm{M,M}) - J(\mathrm{M,X}) = I_X - A_M - J(\mathrm{M,X}), \quad (2)$$

where the parameter of interelectronic repulsion $J(\mathrm{M,M})$ is approximately 16 eV times $\langle r^{-1}\rangle$ of the central atom orbital in reciprocal bohr units, whereas $J(\mathrm{M,X})$ is approximately 27 eV times $\langle r^{-1}\rangle$ of the most extended orbital, here the M.O. delocalized on the X atoms. The fine-structure of electron transfer spectra of hexahalide complexes MX_6^{+z-6} has been thoroughly studied[35–39] and optical electronegativities being defined by identifying the excitation energy (2) with

$$[x_{\mathrm{opt}}(\mathrm{X}) - x_{\mathrm{uncorr}}(\mathrm{M})]\ 3.7\,\mathrm{eV}, \quad (3)$$

where the *x* value of the central atom has not been corrected for (minor) effects of spin-pairing energy, etc.

When photo-electron spectra of gaseous halides are measured[40] with 21.2 eV photons, the order of magnitude of the ionization energy of the loosest bound M.O. is 15.4 eV for fluorides, 12.1 eV for chlorides, 11.3 eV for bromides and 10.2 eV for iodides obtained from the expression $(3.7x_{\mathrm{opt}} + 1)$ eV, slightly lower than I for the gaseous halogen atoms (17.42, 12.97, 11.81 and 10.45, respectively). Gaseous VCl_4 has a weak signal at $I = 9.4$ eV due to the single 3*d*-like electron. Among the relatively few 3*d* group complexes with positive oxidation number of the central atom which are sufficiently volatile to be studied by the technique of Turner are the tris(hexafluoroacetylacetonates)[41,42]. M = Al, Sc and Ga show a standard photo-electron spectrum between $I = 10$ and 18 eV which is also found for the other M. In analogy to vanadium (IV) chloride, M = Ti shows

---

[11] C.K.Jørgensen, *Structure & Bonding 1* (1966) 3.

[12] C.K.Jørgensen, *Helv. Chim. Acta*, Fasc. extraord. Alfred Werner, 1967, 131.

[13] C.K.Jørgensen, *Oxidation Numbers and Oxidation States*, Verlag Springer, Berlin 1969.

[14] J.S.Griffith, *The Theory of Transition-metal Ions*, Cambridge University Press, 1961.

[15] C.K.Jørgensen, *Acta Chem. Scand. 12* (1958) 903.

[16] J.H.E.Griffiths, J.Owen and I.M.Ward, *Proc. Roy. Soc.* (London) *A 219* (1953) 526.

[17] C.K.Jørgensen, *Chimia 25* (1971) 109.

[18] C.K.Jørgensen, *Inorg. Chim. Acta Rev.* (Padova) *2* (1968) 65.

[19] C.K.Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford 1962 (2nd printing 1964).

[20] C.K.Jørgensen, R.Pappalardo and H.H.Schmidtke, *J. Chem. Physics 39* (1963) 1422.

[21] C.E.Schäffer and C.K.Jørgensen, *Mol. Physic 9* (1965) 401.

[22] C.K.Jørgensen, *J. Physique 26* (1965) 825.

[23] D.W.Smith, *Structure & Bonding 12* (1972) 49.

[24] C.E.Schäffer and C.K.Jørgensen, *Mat. Fys. Medd. Dan. Vid. Selskab 34* (1965) No. 13.

[25] C.E.Schäffer, *Proc. Roy. Soc.* (London) *A 297* (1967) 96.

[26] C.E.Schäffer, *Pure Appl. Chem. 24* (1970) 361.

[27] S.E.Harnung and C.E.Schäffer, *Structure & Bonding 12* (1972) 201 and 257.

[28] C.E.Schäffer, *Structure & Bonding 14* (1973) in press.

[29] C.K.Jørgensen, *Modern Aspects of Ligand Field Theory*, North-Holland Publishing, Amsterdam 1971.

[30] K.Ruedenberg, *Rev. Mod. Physics 34* (1962) 326.

[31] C.J.Ballhausen and H.B.Gray, *Molecular Orbital Theory*, Benjamin, New York 1964.

[32] C.K.Jørgensen, *Orbitals in Atoms and Molecules*, Academic Press, London 1962.

[33] C.K.Jørgensen, S.M.Horner, W.E.Hatfield and S.Y.Tyree, *Int. J. Quantum Chem. 1* (1967) 191.

[34] V.Valenti and J.P.Dahl, *Acta Chem. Scand. 20* (1966) 2387.

[35] C.K.Jørgensen, *Progr. Inorg. Chem. 12* (1970) 101.

[36] C.K.Jørgensen and W.Preetz, *Z. Naturforsch. 22a* (1967) 945.

[37] B.D.Bird, P.Day and E.A.Grant, *J. Chem. Soc.* (A) *1970*, 100.

[38] C.K.Jørgensen, W.Preetz and H.Homborg, *Inorg. Chim. Acta* (Padova) 5 (1971) 223.

[39] S.P.Piepho, J.R.Dickinson, J.A.Spencer and P.N.Schatz, *Mol. Physics 24* (1972) 609.

[40] D.W.Turner, C.Baker, A.D.Baker and C.R.Brundle, *Molecular Photoelectron Spectroscopy*, Interscience, London 1970.

[41] S.Evans, A.Hamnett and A.F.Orchard, *J. Coord. Chem. 2* (1972) 57.

[42] S.Evans, A.Hamnett, A.F.Orchard and D.R.Lloyd, *Disc. Faraday Soc. 54* (1973).

Table 1. Ionization energies in eV of the $4f$ shell in solid compounds. Shoulders in parentheses. The quantities I^*, I and I' are defined in the text. Some measurements have been repeated in order to study the reproducibility. Values marked [Mg] have been determined with a new high-intensity X-ray source including a magnesium anti-cathode

	$I^*(\mathrm{M}\,4f)$	$I(\mathrm{M}\,4f)$	$I'(\mathrm{M}\,4f)$		$I^*(\mathrm{M}\,4f)$	$I(\mathrm{M}\,4f)$	$I'(\mathrm{M}\,4f)$
EuF_3	12.7	17.5	13.7	ErF_3	14.2,(11.2)	18.7,(15.7)	15.2,(12.2)
$Eu_2(SO_4)_3$	11.5	16.0	14.0	ErF_3	15.6,(12.3)	20.3,(17)	15.3,(12)
Eu_2O_3	10.4	14.9	12.0	ErF_3 [Mg]	15.3,(12.0)	20.5,(17.2)	15.3,(12.0)
$EuSO_4$	4.5	8.9	6.9	Er_2O_3	12.8,(9.3)	17.5,(14)	14.4,(11)
GdF_3	14.5	18.9	15.3	Tm_2O_3	12.6,(8.5)	17.7,(13.6)	14.9,(10.8)
GdF_3	15.0	19.7	15.6	Tm_2O_3	12.7,(9.2)	16.9,(13.4)	14.3,(10.8)
$Gd_2(SO_4)_3$	12.7	17.5	15.2	YbF_3	15.8,12.0	20.5,16.7	18.0,14.2
Gd_2O_3	11.6	15.6	13.6	Yb_2O_3 [Mg]	12.5,8.8	17.9,14.2	16.4,12.7
TbO_2: Tb(IV)	22.4	27.8	24.7	$Yb_2Hf_2O_7$	14.0,10.3	18.7,15.0	16.2,12.5
Tb(III)	13,(7)	18,(12)	15,(9)	$YbVO_4$	13.3,9.4	18.2,14.3	16.1,12.2
Tb_4O_7: Tb(IV)	21.9	27.0	24.4	LuF_3	15.0	20.5	15.3
Tb(III)	12.1,6.0	17.2,11.1	14.6,8.5	LuF_3	14.8	19.7	15.2
$Tb(OH)_3$	13.0,6.4	18.1,11.5	15.5,8.9	Lu_2O_3	11.2	16.0	13.9
Dy_2O_3	13.6,10.4,(8.0)	17.9,14.7,(12.3)	14.7,11.5,(9.1)	K_2HfF_6	(22.5),21.0	(27.5),26.0	(25.2),23.7
Ho_2O_3	12.0,(8)	16.9,(13)	14.3,(10.4)	$Yb_2Hf_2O_7$	(21.4),19.7	(26.1),24.4	(23.6),21.9

an additional signal at $I = 8.0$ eV, M = V at 8.7 eV due to the two $3d$-like electrons, and M = Cr at 9.6 eV. As one might also extrapolate from the regular development of the electron transfer spectra[43] of acetylacetonates from Ti (III) to Co (III), the I-values of the $3d$-like electrons occur for M = Fe and Co inside the interval of M.O. close to 11 eV. It is not explicitly stated by the authors from Oxford[41, 42] that the two bonding M.O. having the same symmetry type as the higher sub-shell containing each an electron in the high-spin ($S = {}^5/_2$) iron (III) complex, actually has a lower I than the latter sub-shell. It is clear, however, that this cannot be far from the thruth. Anyhow, it is beyond discussion that in most $4f$ group compounds, the anti-bonding (and all the seven) $4f$ orbitals have higher I than the bonding M.O. of the same symmetry type.

This unexpected situation was found independently by workers at the Bell Telephone Laboratory[44] and by us[45, 46], in both cases using a Varian IEE-15 photo-electron spectrometer bombarding solid samples with 1486.6 eV photons. WERTHEIM *et al.*[44] studied fluorides and did not want to pronounce themselves about the absolute ionization energies relative to vacuo because of the *charging effects* discussed below, but they demonstrated that $I(\mathrm{Pr}\ 4f)$ is below $I(\mathrm{F}\ 2p)$ in PrF_3 whereas $I(\mathrm{M}\ 4f)$ and $I(\mathrm{F}\ 2p)$ coincide in slightly heavier lanthanides. Table 1 gives values measured by us. I^* is the value recorded by the instrument as the difference between 1482 eV (in the case of 1253.6 eV photons originating in a magnesium anti-cathode, 1249 eV) and the kinetic energy of the photo-electrons at the peak. I^* is intended to refer to a common FERMI level of the apparatus 4.6 eV though this argument is unsatisfactory for non-conducting samples. I is the value obtained[45] by using the carbon $1s$ signal of scotch tape as internal reference 290.0 eV. This means adding to each I^* value a correction C_{st} obtained for a given sample as the difference between 290 eV and the lowest $I^*(\mathrm{C}\,1s)$ detected. The disadvantage of this treatment is that non-conducting samples frequently (but not in the case of conjugated constituents such as tetraphenylborates and tetraphenylarsonium and methylene blue salts) acquire a quasi-stationary positive potential between 2 and 5 V, the most positive values occurring for certain anhydrous fluorides. It can be argued[47] that this potential can be measured as the difference ∂ between the two carbon $1s$ signals, and I' defined as the difference between I and ∂ should be a better approximation to the ionization energy in neutral solids relative to vacuo. A major argument for the validity of this treatment[47] is that I' is reproducible with an average difference of only 0.2 eV, whereas I according to circumstances scatter between a-half and one eV. In all the samples given in Table 1, ∂ and I' could be determined. When compared with the I' values of ionic fluorides usually between 12 and 13 eV (slightly lower than gaseous fluorides[40]) it is clear[44] that most of the $I'(\mathrm{M}\ 4f)$ are larger, in particular for the half-filled shell Gd (III). The same is true for the oxides, where both $I'(\mathrm{M}\ 4f)$ and $I'(\mathrm{O}\ 2p)$ are slightly smaller. The difficulty is here that the signals of different shells have relative intensities[48] differing by a factor 1000. Oxygen $2p$ gives a very weak signal, but the values $I^* = 10$ eV, $I = 14$ eV and $I' \approx 10.4$ eV have been determined for MgO, and comparable values[47] for Cr_2O_3 and ThO_2.

For a given number of $4f$ electrons, the ionization energies increase 9 eV going from M (II) to M (III) or from M (III) to M (IV). This is a major factor in understanding the specific behaviour of the lanthanides[49]. As a function of the number of $4f$ electrons, the variation agrees with the spin-pairing energy theory[13, 29] of interelectronic repulsion having the parameter $D = 0.8$ eV (already known from absorption spectra[32]) and $(E - A) = 0.4$ eV. Actually, the uncorrected optical electronegativities $x_{\mathrm{uncorr}}(\mathrm{M})$ evaluated[50] for M (IV) [the final state of ionization of one $4f$ electron from M (III)] give 13.6 eV for M = Eu, 15.1 eV for Gd, 10.2 eV for Tb, 12.1 eV for Dy, 13.2 eV for Ho, Er and Tm, 14.3 eV for Yb and 16.2 eV for M = Lu in excellent agreement with the I' values of

Table 1 when the expression $(1 + 3.7\ x_{\text{uncorr}})$ eV mentioned above for halide ligands is assumed. The multiple signals for eight to thirteen 4*f* electrons can be explained with the treatment of the probability of forming different states of $4f^{q-1}$ as later discussed with Cox. By the same token, $x_{\text{uncorr}} = 1.9$ for Eu (III) suggests $I' = 8.0$ eV for europium (II) compounds in reasonable agreement with $I' = 6.9$ eV found for $EuSO_4$. It may be mentioned that the chemical ionization energy I_{chem} derived[13, 51] from the sum of 4.5 eV and the standard oxidation potential of the aqua ions is 4.1 eV for Eu (II). The discrepancy from the value observed for $EuSO_4$ may, in part, be due to high stability of the latter crystal, but a more important effect is that the very rapid photo-ionization, like visible spectra, obeys the FRANCK-CONDON principle of not changing the internuclear distances. The photo-electron spectra of gaseous molecules[40] show co-excitation of complicated vibrational structure for this reason. Since the resolution of X-ray induced photo-electron spectra is not much better than 1 eV, the result is mainly a broadening (*e.g.* of the 1*s* signals of lithium and certain nitrogen and oxygen compounds[47]). Quite generally, anions tend toward larger half-widths possibly because of the more important change of equilibrium ionic radius by ionization[52]. On the other hand, standard oxidation potentials refer to an adiabatic process allowing great changes of the internuclear distances. Actually, it is known from kinetic isotope experiments that the electron exchange between Eu (II) and Eu (III) aqua ions is rather slow.

It is also possible to determine I^* (M 4*f*) relative to the FERMI level of metallic lanthanides[53]. Thus, $I^* = 7.8$ eV for gadolinium corresponding to an absolute $I = 11.0$ eV may be compared with the I' values in Table 1. In the case of metallic europium and ytterbium[53], I^* is much smaller and close to 2 eV, and hence, I is between 4 and 5 eV only. It is rather fascinating that the conduction electrons do not invade the 4*f* orbitals having a positive I^*, but it is again a question of the low electron affinity of the 4*f* shell having a small average radius. It is possible to compare photo-electron spectra with X-ray emission and absorption spectra of the lanthanides and their compounds[54].

The main paradox derived from these new results is that the ionized system M (IV) lacking a 4*f* electron present in the groundstate of M (III) is almost degenerate in energy with the fluoride or oxide ligands lacking a 2*p* electron. In all models related to the ideas of HÜCKEL, this is the essential condition for strong covalent bonding. But it is perfectly known from the weak nephelauxetic effect in lanthanide compounds[13, 29, 32] that both the symmetry-restricted and central-field covalency is unusually weak. It is not trivial to note that the transferable parameters of the angular overlap model for 4*f* compounds[20, 55] have the sign expected for σ-anti-bonding effects (and not bonding corresponding to the back-bonding to empty ligand orbitals in carbon monoxide complexes). Further on, the σ-anti-bonding effects described in the angular overlap model change in a very smooth way[20] from Ce (III) to Yb (III) and do not show the discontinuities one would expect from a crossing of I_M and I_X at one or three positions in this series.

The way out of this conceptual labyrinth is to realize that the total wave-function Ψ has its energy minimized in a variational treatment, but not necessarily the one-electron functions. The behaviour of the individual orbitals is symphonically coupled through the two-electron operator of interelectronic repulsion. In this sense, it is perfectly conceivable that the orbital energy differences in a given *l*-shell used for parametrization in "ligand field" theory are purely accounting quantities and carry no clear relation with ionization energies. Even without introducing correlation effects, the *J*-integrals of interelectronic repulsion destroy the additivity of one-electron energies in electron configurations[13] (thus, the baricenter of $2s\,2p$ has a lower energy than the mean value of $2s^2$ and the baricenter of $2p^2$) and the fact that most neutral transition-group atoms have a lowest electron configuration containing one or two *s* electrons which are removed at first by ionization can be explained by the simple model[56] of the phenomenological baricenter polynominal. The situation is rather similar to the pool of conduction electrons in metallic lanthanides co-existing with a definite number of 4*f* electrons determining[13] the conditional oxidation state, such as Eu [II] and Gd [III].

It might be argued that the diagonal elements of a one-electron model are not intended to indicate ionization energies I but rather the average value $(I + A)/2$ with the electron affinity A used by MULLIKEN in his definition of the electronegativity[32]. If the *J*-integrals expressing the main part of $(I - A)$ according to eq. (2) are almost identical in carbon and nitrogen, this would still be compatible with a HÜCKEL description. Then, the covalent bonding in lanthanide compounds is not expected to be pronounced, because $(I - \frac{1}{2}J) = (A + \frac{1}{2}J)$ of X is considerably larger than of M.

---

[43] C. K. JØRGENSEN, *Acta Chem. Scand. 16* (1962) 2406.

[44] G. K. WERTHEIM, A. ROSENCWAIG, R. L. COHEN and H. J. GUGGENHEIM, *Physic. Rev. Letters 27* (1971) 505.

[45] C. K. JØRGENSEN, *Chimia 25* (1971) 213 and *26* (1972) 252.

[46] C. K. JØRGENSEN, *Theoret. Chim. Acta 24* (1972) 241.

[47] C. K. JØRGENSEN and H. BERTHOU, *Mat. Fys. Medd. Dan. Vid. Selskab 38* (1972) No. 15.

[48] C. K. JØRGENSEN and H. BERTHOU, *Disc. Faraday Soc. 54* (1973) 269.

[49] C. K. JØRGENSEN, *Structure & Bonding 13* (1973) 199.

[50] L. J. NUGENT, R. D. BAYBARZ, J. L. BURNETT and J. L. RYAN, *J. Inorg. Nucl. Chem. 33* (1971) 2503.

[51] C. K. JØRGENSEN, *Chimia 23* (1969) 292.

[52] P. H. CITRIN and T. D. THOMAS, *J. Chem. Physics 57* (1972) 4446.

[53] P. O. HEDÉN, H. LÖFGREN and S. B. M. HAGSTRÖM, *Physic. Rev. Letters 26* (1971) 432.

[54] C. BONNELLE, R. C. KARNATAK and C. K. JØRGENSEN, *Chem. Physic. Letters 14* (1972) 145.

[55] G. BURNS, *Physic. Letters 25A* (1967) 15.

[56] C. K. JØRGENSEN, *Angew. Chem. 85* (1973) 1 [*Intern. Ed. 12* (1973) 12].

However, it seems more probable that one has to perform an iteration when estimating the extent of covalent bonding between atoms having highly different J-integrals. The idea of an iteration is not foreign to the Wolfsberg-Helmholz model either[31]. Thus, when describing the vanadyl ion $VO(H_2O)_4^{+2}$ an interpolation of energies and overlap integrals until a consistent distribution of fractional atomic charges is performed. This interpolation is not too dangerous[33] except for the oxide ion not possessing a Hartree-Fock function. Only in the presence of a strong Madelung potential, the species O^{-2} does not loose an electron spontaneously. When the covalent bonding is pronounced, the diagonal elements involve the same parameter [whether it being $(I+A)/2$ or I] of M and of X, whereas in our case of almost ionic lanthanide compounds, the weak covalent bonding is determined by a comparison between A_M and I_X. This has a certain connection with the suggestion[82] that the electronegativities of the M and X atoms are equilibrated in the former, strongly covalent case, whereas it is impossible that they are equilibrated in the latter case frequent in transition-group chemistry.

Even considering $4f^8$ dysprosium (IV) in Cs_3DyF_7, no partly filled shell in any chemical compound has a higher ionization energy than terbium (IV). I' close to 24 eV in Table 1 actually indicates that terbium (V) cannot exist. When neglecting the comparatively minor effects of changing the internuclear distances, the electron affinity of Tb (V) would be 24 eV, and this oxidation state would be able to oxidize helium and the other noble gases, or for that matter, potassium salts to K (II) because it is known from photo-electron spectra[47, 57] that I'(K $3p$) usually is between 21 and 23 eV. On the other hand, the electron affinity of terbium (IV) is approximately the ionization energy of Tb (III) of which I' is close to 9 eV in Table 1. Hence, terbium (IV) compounds are expected to be rather covalent, and as confirmed by the chemical behaviour, incompatible with reducing ligands.

Koopmans pointed out in 1933 that the one-electron energies for a Hartree-Fock function have the property that they would represent the ionization energies of the system (with opposite sign) if the orbitals of the other electrons did not *contract* under the influence of the modified central field. In M. O. calculations, the observed deviations from Koopmans behaviour can be described, by a rule of thumb, as 8 percent lower I than the calculated values (in the valence region for I below 50 eV). The inner shells with I below 1400 eV of interest to our brand of photo-electron spectrometry have deviations amounting to approximately the square-root of I by some odd accident. In a sense, the difficulties for "ligand field" theory discussed here are also due to deviations from Koopmans behaviour. In such a compound where I' of the ligand orbitals and I' (M $4f$) in Table 1 coincide exactly, the ionized system is highly covalent corresponding to a large reorganization of the M. O. The chemical shifts of ionization energies of inner shells[47, 57] also show an inter-atomic Manne effect[58] that the adaptation of the electronic density of the neighbour atoms contributes to a significant decrease of I.

Rather than presenting three consecutive cataclysms overrunning "ligand field" theory it is also possible to paint a picture of a much more continuous evolution[59] based on the symmetry and group-theoretical arguments entering the problem. However, the recent observations of "vertical" ionization energies of penultimate M. O. and inner shells clearly open the rather terrifying question whether quantum mechanics has the unique utility to chemists of supplying phenomenological models. The only species better known from approximate solutions to the Schrödinger equation are of the type H_3^+, H_4^+, HeH^+, HeLiH, CH_4^+, CH_5^+ and ArF^+. Exactly as the two-electron operator quantities are strongly modified by the Watson effect[32], the parameters of "ligand field" theory should rather be called *sub-shell energy differences* and not brought in direct connection with genuine ionization energies (which were unknown previously) and their differences. It has been too common in "ligand field" theory to filter off the mosquito and swallowing the camel.

Acknowledgments. The grant for purchase of the photo-electron spectrometer and its additional high-intensity magnesium X-ray source was provided by the Swiss National Science Foundation. I am grateful to my collaborators Dr. Hervé Berthou and Dr. Lucette Balsenc for their careful work and to Professor Georg Brauer, Freiburg im Breisgau, for a sample of TbO_2 and to Professor Cornelius Keller, Karlsruhe, for LuF_3.

[57] C. K. Jørgensen, H. Berthou and L. Balsenc, *J. Fluorine Chem. 1* (1972) 327.

[58] C. K. Jørgensen, *Adv. Quantum Chem. 8* (1973) in press.

[59] C. E. Schäffer, *Wave Mechanics—the first Fifty Years* (editors: S. S. Chissick, W. C. Price and T. Ravensdale) chapter 12, p. 174, Butterworths, London 1973.