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The Interelectronic Repulsion Integrals and the Purity of Molecular Orbital Configurations, as Derived from the Absorption Spectra of Transition Group Complexes

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The ligand field theory has made several steps of increasing generality regarding the partly filled shell in transition group complexes. The electrostatic model, where the radial function is not varied, is disproven by the nephelauxetic series (see eqn. 8), where the term distances are decreased, relative to the gaseous ions. It is here shown that the two possibilities: expanded radial functions of a *d*-shell, with appropriate angular dependence, or a molecular orbital theory with an integral number of γ_3 and γ_5 electrons, but without the assumption of $l = 2$, give nearly identical results of the interelectronic repulsion integrals, separating the levels of a given sub-shell configuration. Tanabe and Sugano's theory and the role of configuration intermixing in complexes and gaseous ions is discussed, and it is concluded that the number of electrons in the partly filled shell of a monomeric complex is very well defined.

Slater, Condon, and Shortley [1] demonstrated that it is a rather good approximation to the wavefunction of gaseous atoms and ions to assume well-defined electron configurations, *i.e.* an integral number between 0 and $4l + 2$ electrons in each *nl*-shell, by writing the wavefunction as the anti-symmetrized product of one-electron functions

$$\psi = \frac{1}{r} \cdot R_{nl}(r) \cdot A_l(\varphi,\vartheta) \tag{1}$$

where the angular part A_l is a linear combination of the angular functions known from the theory of the hydrogen atom, while the radial part R_{nl} is not at all hydrogen-like, but must be determined, *e.g.* by Hartree's methods, for each atomic number Z and ionic charge $Z_0 - 1$. If the electron configuration contains at least one partly filled shell (with l at least 1), it corresponds to several energy levels, which in Russell-Saunders coupling can be assembled in multiplet terms, characterized by definite values of the quantum numbers L and the total spin S. The fine structure of the multiplet terms, giving energy levels with different J, is caused by electrodynamic (*i.e.* magnetic) and relativistic effects and is proportional to the Landé factors ζ_{nl}. The energy differences between the LS-terms are caused by the electrostatic repulsion between the electrons in the partly filled shell. This repulsion depends even for identical R_{nl} and thus identical attraction by the nucleus on the angular distribution A. In the case of one partly filled l-shell, the relative energy differences are expressed [1] as linear combinations of the integrals F^2, F^4, . . . , F^{2l}, which are approximately [2] inversely proportional to the average distance from the nucleus. The much larger contribution $\frac{1}{2}\mathrm{q}(\mathrm{q}-1)F^\circ$ is identical for all terms of a given configuration and can be considered as the spherical symmetrical average of the electrostatic repulsion between the q electrons in the partly filled shell, just as the central field from the electrons in closed shells, which determines the radial function R_{nl}.

In systems with several nuclei, *i.e.* in molecules and complex ions, the nl-shells are substituted by molecular orbitals γ_n, and the LS-terms are substituted by energy levels, characterized by Γ_n and S. The quantum numbers γ_n and Γ_n are found by group theoretical methods and depend on the symmetry of the complex. Thus, in the symmetry $\mathrm{O_h}$ (that of cubes and regular octahedrons [3]) the wavefunctions must obey certain conditions when performing the transformations of the group (such as rotations of the system of coordinates around the axes of the complex *etc.*). In this way, the wavefunctions always fall in one of the ten classes γ_n (electrons) or Γ_n (whole systems), where n = 1, 2, 3, 4, or 5, and the parity is odd or even. However, in molecules, the approximation of molecular orbital configurations is not as generally valid as in the gaseous ions placed in the high symmetry of empty space. The principal purpose of this paper is to study whether this approximation seems to be valid in octahedral complexes of the three transition groups, where the absorption spectra recently have been interpreted by ligand field theory [4-11].

Even though the intermixing of molecular orbital configurations presents much difficulty, *e.g.* in the aromatic hydrocarbons [12,13], its extent has not generally been recognized in chemical textbooks. For large internuclear distances in H_2 or O_2, the configurations are highly intermixed and do not correspond much to the equilibrium groundstate [14]. Since the covalent bonding in $\mathrm{d^n}$-complexes does not depend alone on the behaviour of the partly filled shell, similar conditions might prevail there. Another feature of particular importance for $\mathrm{d^n}$-complexes is the electrostatic repulsion between the d-electrons, producing the same correlation effects as those mentioned above in the gaseous ions. Actually, the relevant multiples of F^2 and F^4 have the same order or magnitude as the ligand field parameter Δ (also called (E_1-E_2) or 10 Dq) which is the energy difference between the γ_3- and the γ_5-subshell. Therefore, it is not always valid to assume the groundstate to have the maximum number of γ_5-electrons possible, even though γ_5 has lower orbital energy than γ_3. In the case of $\mathrm{d^4}$, $\mathrm{d^5}$, $\mathrm{d^6}$, and $\mathrm{d^7}$, this would produce states with lower values of S, *i.e.* magnetically anomalous complexes, than has the gaseous ion. However, this is only possible, when the spin-pairing energy [6,8,15], *i.e.* an appropriate linear combination of F^2 and F^4, is smaller than Δ.

Theoretically, the electrostatic repulsion energies can be found in molecular orbital theory as sums of four-electron integrals

$$(\mathrm{a\ b}\ g\ \mathrm{c\ d}) = \int\int \Psi_{\mathrm{a}}^{*}(\tau_1)\Psi_{\mathrm{b}}^{*}(\tau_2)\ \frac{e^2}{r_{12}}\ \Psi_{\mathrm{c}}(\tau_1)\Psi_{\mathrm{d}}(\tau_2)\ \mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (2)$$

which has the physical significance of the electrostatic interaction between two extended charge distributions $\Psi_{\mathrm{a}}^{*}\Psi_{\mathrm{c}}$ and $\Psi_{\mathrm{b}}^{*}\Psi_{\mathrm{d}}$. If the diagonal element of g for a given configuration is wanted, it is only necessary to use two types of two-electron integrals:

$$\mathrm{J(ab)} = (\mathrm{ab}\ g\ \mathrm{ab}) \text{ and } \mathrm{K(ab)} = (\mathrm{ab}\ g\ \mathrm{ba}) \qquad (3)$$

where a summation is performed over all pairs ab in the configurations, and with negative sign of the K-integrals, when they do not vanish. Since (2) vanishes *, if a and c do not have the same spin component m_s, or if b and d do not have the same m_s, the results will be for each pair

$$\begin{array}{llll} \mathrm{a^+b^+} & : \mathrm{J(ab) - K(ab)} & \mathrm{a^+a^-} & : \mathrm{J(aa)} \\ \mathrm{a^+b^-} & : \mathrm{J(ab)} & \mathrm{b^+b^-} & : \mathrm{J(bb)} \\ \mathrm{a^-b^+} & : \mathrm{J(ab)} & & \\ \mathrm{a^-b^-} & : \mathrm{J(ab) - K(ab)} & & \end{array} \qquad (4)$$

Since the wavefunctions usually do not need to be chosen as complex functions, the asterisks in (2) denoting complex conjugation will generally be superfluous, and in this case, the following relation will be valid:

$$(\mathrm{aa}\ g\ \mathrm{bb}) = (\mathrm{ab}\ g\ \mathrm{ba}) = \mathrm{K(ab)} \qquad (5)$$

representing the interaction of the charge distribution ab with itself, while J(ab) still is the classical interaction between the actual electron densities a^2 and b^2. It may be remembered that the integral of ab over the total space is zero and of a^2 equal to one, being the orthogonalization and normalization conditions, respectively.

The electrostatic energies can now be found as the eigenvalues of determinants having as diagonal elements the molecular orbital configurations with given spin directions m_s (+ and − in eqn. 4) and identical values of M_s. The problem of an electronic configuration with two electrons with $l = 0$ and a higher value, as treated by Heisenberg in case of the excited

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* Further, it is a group-theoretical requirement for (2) not to vanish that abcd contains the representation Γ_1, since g is a totally symmetric operator. This is equivalent to the condition that ac and bd have the same Γ_n in their products as applied p. 911.

states 1s *nl* of a helium atom *, and by Houston as a general problem with intermediate coupling in heavy atoms, corresponds to a determinant for $M_s =$ 0 with two equal diagonal elements J(ab) of eqn. 4 and the non-diagonal element K(ab), having as eigenvalues the triplet energy J(ab)—K(ab) and the singlet energy J(ab) + K(ab). Below, the similar problem with three identical diagonal elements J and three non-diagonal elements $\pm$ K is of interest. If an odd number of the non-diagonal elements is + K, the eigenvalues will be J + 2K, J — K, and J — K, while if an even number has the positive sign of K, the eigenvalues will be J — 2K, J + K, and J + K. Generally, a determinant with q equal diagonal elements = J and all the $\frac{q}{2}(q-1)$ non-diagonal elements = K will have the eigen-value J + (q — 1)K and (q — 1)-fold the eigen-value J—K.

The determinant with a given value of M_S can be divided in subdeterminants, each being diagonal in a group-theoretical quantum number Γ_n appropriate to the symmetry, where all the orbitals a and b have different γ_n. Unfortunately, this is not possible in O_h, where the three degenerate γ_5-orbitals do not necessarily have the same electrostatic interaction with the two γ_3-orbitals. This difficulty can be removed by considering lower symmetries, such as tetragonal or rhombic, without altering the energies of the orbitals belonging to the same cubic γ_n. Mr. Schäffer has kindly informed me that there exist essentially different forms of rhombic symmetry, while the difference between the two tetragonal symmetries I and II (Ref.[16], p. 6) has no physical significance. The rhombic symmetry I is a case of C_{2v} with the two-fold axis and the two two-fold mirror axes in the direction of the ligands (being placed on the x,y,z-axes) while II is another C_{2v} with the z-axis still as the two-fold axis, but the two two-fold mirror axes along the lines x + y and x — y in the xy-plane. The behaviour of the five orbitals is then:

	tetragonal	rhombic I	rhombic II
cubic 3	1 + 3	1 + 1	1 + 3
cubic 5	4 + 5	2 + 3 + 4	1 + 2 + 4]

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* The following Table indicates the ratio T in per cent between the triplet-singlet distance, *viz.* 2K(ab) = 2 G_1 in Slater integrals[1] and the energy of the triplet-singlet midpoint, *viz.* the orbital *nl*-energy, for a set of series of He, Li+, and Be. Further, T is shown to be approximately inversely proportional to the principal quantum number *n*:

	n =	2	3	4	5	6	7	8
He 1s *n*s	T =	18.22	11.42	8.35	6.59	5.44	4.63	4.04
	nT	36.44	34.25	33.39	32.93	32.64	32.42	32.32
He 1s *n*p	T =	7.26	5.22	3.96	3.19	2.66	2.29	2.00
	nT	14.52	15.65	15.84	15.96	15.98	16.03	15.98
Li+ 1s *n*s	T =	10.80	7.54	5.49	4.35	3.55	3.06	—
	nT =	21.59	22.61	21.96	21.74	21.30	21.39	—
Li+ 1s *n*p	T =	6.45	4.55	3.37	2.82	—	—	—
	nT =	12.89	13.63	13.49	14.08	—	—	—
Be $1s^2 2s$ *n*d	T =	—	19.94	12.26	9.02	7.23	5.85	5.25
	nT =	—	59.82	49.06	45.08	43.36	40.99	41.96

Since the orbital energies are inversely proportional to $(n+\delta)^2$, where δ is the Rydberg correction, the exchange integrals K(ab) are shown to vary nearly as n^{-3}, as mentioned by Van Vleck[30].

These group-theoretical results are very useful for the following arguments, when it is no longer supposed that the molecular orbital can be written as eqn. 1, *i.e.* that l is no longer well-defined. In most cases, it will be a linear combination of different radial and different angular functions, such that a separability into a product R·A will not be possible. In this case, the expansion of the electrostatic energy in a series of F^k-contributions (k = 0, 2, 4, ...) will no longer terminate, but contain members with very high k.

The ligand field theory has applied more or less refined approximations in the description of d^n-complexes, of which a fair selection would be:

1. First-order perturbation energy on A is considered, but only the diagonal elements of weak field (assuming well-defined L) or strong field (assuming well-defined sub-shell configuration $\gamma_5^a\gamma_3^b$) determinants are considered.

2. The same as 1, but the restriction of sharply defined L or $\gamma_5^a\gamma_3^b$ removed, such that the energy levels are eigenvalues of determinants of q'th degree, if q levels present the same combination of S and Γ_n. The theory has thus one parameter Δ, assuming fixed atomic term distances, and can be expressed as in the Orgel-diagram [6].

3. Besides the first-order perturbation energy on A, there subsist second-order perturbations on R, changing the central field and thus the radial function R. But there is still assumed hydrogen-like A, *i.e.* $l = 2$. The theory has two types of parameters, Δ and the relative decrease of F^k- integrals in complexes, relative to those of the gaseous ion and can be expressed in the Tanabe-Sugano-diagram [5], where the independent variable is Δ : B. The ratio between $B = 1/49\ F^2 - 5/441\ F^4$ and $C = 5/63\ F^4$ is assumed to be constant $\sim 1/4$.

4. The molecular orbitals γ_3 and γ_5 are not assumed to have the same radial function, but still the set of A corresponding to $l = 2$. Thus, the parameters B and C change in each sub-shell configuration $\gamma_5^a\gamma_3^b$.

5. The molecular orbitals are even not assumed to have hydrogen-like angular dependence, but their configurations are assumed to be rather well-defined. In this case, the different J- and K-integrals are applied, as outlined above, in the place of B and C.

6. The complete molecular orbital theory is presumed with large intermixing of configurations.

Of these approximations, 1 is obsolete, as are also the discussions of whether a given complex could be said to have strong or weak ligand field (incidentally, the best agreement is obtained in nearly all complexes with the former type of diagonal elements). It was often overseen that also the strong field diagonal elements contain multiples of F^k besides the multiples of Δ, and some misleading remarks were made about the complete "quenching" of the interelectronic repulsion for $\Delta \rightarrow \infty$.

Approximation 2 concentrated the interest on Tsuchida's spectrochemical series, *i.e.* the variation of Δ as a function of the ligands for a given metal ion:

$$\mathrm{Br^- < Cl^- < F^- < urea < ox^{--} \lesssim H_2O < SCN^- < NH_3 < en \ll CN^-} \tag{6}$$

while the series as function of the central ion for the same ligand is:

$$\mathrm{Mn(II) < Ni(II) < V(II) < Fe(III) < Cr(III) < Co(III) < Mo(III) < Rh(III) < Ir(III) < Pt(IV)} \tag{7}$$

The most characteristic property of the "electrostatic model" of ligand fields is that the radial function is not made subject to a variation. However, the series (6) was nearly incredible as a result of a purely electrostatic effect of the ligands, and it was soon proposed [6,9] to re-investigate Van Vleck's old remark [17] that the intermixing of orbitals with the same γ_n and parity from the central ion and the ligands, *i.e.* partly covalent bonding in the L.C.A.O. description, might as well explain * the magnitude of Δ, which was a successful empirical parameter rather than an absolute result of the electrostatic model (where the hydrogen-like radial functions and point dipoles necessarily must imply wrong results [8]). Thus, the low values of Δ in halide complexes was now ascribed to π-bonding effects, which increase the energy of the anti-bonding γ_5-orbital, while σ-bonding and electrostatic effects tended to increase Δ.

The first reliable method of estimating the relative extent of the partly covalent bonding from the absorption spectra appeared, when it was realized that the approximation 3 very nearly describes the observed energy levels. It has, however, been a general error by most investigators (including the present author) of d^n-complexes, to draw the opposite conclusion that no other explanation could reasonably be valid, if a given model worked quite well. It is actually possible to arrange the complexes in a two-dimensional system, according to Δ and to $\beta = B_{\text{complex}} : B_{\text{gaseous ion}}$. Schäffer and the present author [18] have studied the nephelauxetic ** series, *i.e.* the tendency to decrease β below 1 as a function of the central ion (giving nearly the same series as (7) except that Mo(III) is placed before and Fe(III) after Cr(III)) and of the ligands:

$$F^- > H_2O > \text{urea} > NH_3 > \text{en} \gtrsim \text{ox}^{--} > SCN^- > Cl^- \gtrsim CN^- > Br^- \qquad (8)$$

which is quite different from (6). The nephelauxetic series corresponds to the general opinion about the relative tendency towards covalent bonding, and it corresponds nearly to the hyperchromic series [19,20] of increasing inten-

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* The absolute magnitude of Δ can also be estimated from the intermixing of molecular orbitals (from the ligands and the central ion) with the same γ_n and parity, assuming known diagonal elements of energy, and non-diagonal elements proportional to known overlap integrals multiplied by the average of the two diagonal elements. There is no doubt that reasonable agreement can be obtained by this form of approximation No. 5 choosing among an infinite set of assumed diagonal energies and overlap integrals (which in most papers refer to the un-realistic hydrogen-like radial functions). However, the three interesting attempts [34-36] to explain the absorption spectra without making any allusion to the electrostatic model No. 2 have all neglected the interelectronic repulsion integrals, separating the levels of the same molecular orbital configuration. Especially, the recent treatment [36] of $Co(NH_3)_5Cl^{++}$ and $Co(NH_3)_4Cl_2^+$ have ascribed the distance, occurring in $Co(NH_3)_6^{+++}$ between $^1\Gamma_4$ and $^1\Gamma_5$, to the energy difference between the σ-anti-bonding orbitals γt_3 and γt_1. An erroneous extension of this thought [36] has necessitated the identification of the two first bands of trans-$Co(NH_3)_4Cl_2^+$ as transitions to $^1\Gamma t_5$ and $^1\Gamma t_4$, *i.e.* implying $^1\Gamma_5$ in O_h, as originally supported by the electrostatic model of ligand fields[16]. The molecular orbital theory for D_{4h} explains the actual behaviour[23] assuming π-bonding from the halide ligands. There is no doubt that a very fine description could be obtained by taking also the interelectronic repulsion integrals into account, if the first-order perturbations on the diagonal elements could be reasonably estimated. *Cf.* the recent treatment of cobalt(III) complexes by Yamatera [37].

** The word »nephelauxetic» (= cloud-expanding) has been kindly proposed by Professor Kaj Barr, University of Copenhagen.

sities of the Laporte-forbidden d^n-transitions and to decreasing oxidation potential of the ligands, *i.e.* decreasing energy for the removal of an electron.* All these three properties are undoubtedly connected; the intensities are roughly inversely proportional to the square of the distance in wavenumbers between the ligand field bands and the "redox" electron transfer bands, and the covalent bonding is enhanced by the easy transfer of electrons from the ligands to the central ion. Schäffer [21] investigated a series of chromium(III) complexes with oxygen atoms in the first co-ordination sphere and found a wide distribution in the nephelauxetic series: sulfate has even higher β than water, while most anion complexes and the red ruby fall in middle of the series, and green Cr_2O_3 has even smaller β than $Cr(CN)_6^{-3}$. For all these complexes, Δ does not vary more than between 14 640 and 18 520 K (= cm^{-1}).

Since γ_3-electrons have more repulsive effects on the ligands than γ_5-electrons have, as can be implied from the differences in ionic radii and from the bandwidths, it is obvious to introduce the fourth approximation, p. 907. However, a new difficulty arises: the spin-forbidden bands deliver a linear combination of B and C, while the states with maximum value of S are separated by multiples of B only. Thus, it is not easily decided, whether β_3 is smaller in the γ_3 sub-shell. This problem is discussed in Refs.[22,23]. For the following discussion, it might be useful to classify the experimental evidence, which is used for the determination of Δ and B in the complexes:

Only the Jahn-Teller regular systems are considered, because the determination of β is so sensitive for small irregularities in the wavenumbers. Perhaps, d^2- and d^7-systems might also be studied, while the tetragonal distortions are too large in d^4 and d^8 ($S = 0$). Among the regular systems, Δ can be directly found as the wavenumber ** of the first spin allowed band (when corrected for possible intermixing with spin-forbidden bands) in d^3- and d^8 ($S = 1$) systems. In d^5 ($S = 5/2$) and d^6 ($S = 0$), it is necessary to correct the distances ${}^4\Gamma_4(G) - {}^4\Gamma_{1,3}(G)$ and ${}^1\Gamma_1 - {}^1\Gamma_4$, respectively, for a contribution of F^k- type

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* However, Bailey [38] has recently determined the electron affinity of gaseous fluorine atoms to be between that of chlorine and that of bromine atoms. Thus, the nephelauxetic series and the chemical intuition must be connected with polarizabilities rather than ionization potentials.

** This is only valid until approximation No. 3. As seen from eqns. 14 and 16, the energy difference between ${}^4\Gamma_5$ and ${}^4\Gamma_2$ of d^3 is $\Delta + 2\,\Theta$, where $\Theta = J(3.5) - K(3.5) - J(4.5) + K(4.5)$ (*cf.* eqn. 12). Similarly, the energy difference in d^2 between $\frac{3}{4}\,({}^3\Gamma_5) + \frac{1}{4}\,({}^3\Gamma_4\gamma_5\gamma_3) - ({}^3\Gamma_4\gamma_5^2)$ is $\Delta + \Theta$ (*cf.* eqns. 13 and 15). The quantity Θ is zero in the electrostatic model, but will probably tend to have a negative value in the molecular orbital theory. The most important contributions to Θ comes from the J-integrals (eqn. 10) which contain the Racah parameter A and thus F^0. It will probably be a rather good approximation to assume that the interaction between a γ_3- and a γ_5-electron is decreased ϑ and between two γ_3-electrons decreased 2 ϑ, relative to the interaction between two γ_5-electrons, which are in average concentrated in a smaller volume. If the latter approximation is valid, the value of Δ will always be decreased $(n-1)\,\vartheta$ in a d^n-system. Thus, in this case the same apparent value of Δ will always be implied from one and two-electron transitions. Since F^0 is a large but unknown quantity $\sim$100 000 K, (= cm^{-1}) ϑ will have an important effect on Δ, even if it amounts only to some per cent of F^0. However, the physical significance of F^0 is of analogous nature to the whole self-consistent field influence, which determines the not very accessible orbital energies. Systems as d^8 can profitably be treated as d^{10}-systems, where two positively charged holes occur. The interaction between the ten electrons $\gamma_5^6\gamma_3^4$ is $6\,J(1.3) + 2K(1.3) + 12J(1.4) - 6K(1.4) + 12J(3.4) - 6K(3.4) + 12J\,(4.5) + 3J(4.4) - 6K(4.5)$ which gives a mathematically complicated contribution to the energy of, *e.g.*, a zinc(II) complex.

(*viz.* C), and for effects of sub-shell configuration intermixing, for obtaining Δ. The value of β can be obtained with reasonable accuracy from six classes of energy differences:

${}^4\Gamma_2-{}^2\Gamma_3$, ${}^2\Gamma_4$, ${}^2\Gamma_5$, all of $\gamma_5{}^3$ in d^3. They are the sharp "ruby" lines of Cr(III), Mo(III), and Re(IV) which are nearly independent of Δ. The suppression, due to interaction with other sub-shell configurations is largest for ${}^2\Gamma_5$, while it is smaller for ${}^2\Gamma_3$ and negligible for ${}^2\Gamma_4$. However, ${}^2\Gamma_3$ is distinctly the sharpest transition.

${}^4\Gamma_5(F)-{}^4\Gamma_4(F)$ (and ${}^4\Gamma_4(P)$) of d^3. The two first of the three broad bands yield a value of B directly from the second-degree determinant for ${}^4\Gamma_4$. Schäffer has demonstrated that the third band of Cr(III), when known, often deviates from the prediction contrary to the analogous d^8-case. This effect is perhaps caused by interactions with electron transfer states.

${}^6\Gamma_1(S)-{}^4\Gamma_1(G)$, ${}^4\Gamma_3(G)$ (and also ${}^4\Gamma_5(D)$, ${}^4\Gamma_5(D)$, and ${}^4\Gamma_2(F)$) of $\gamma_5{}^3\gamma_3{}^2$ in d^5. The two first quartet levels [*] are degenerate for $l = 2$ and produce the sharp band[39] of Mn(II) and Fe(III). They are independent of Δ to a high approximation[*] and indicate $10B + 5C$.

${}^1\Gamma_4-{}^1\Gamma_5$ of $\gamma_5{}^5\gamma_3$ in d^6. This distance between the two first spin-allowed bands of diamagnetic Co(III), Rh(III), and Ir(III) complexes is $16B$ for $\Delta \to \infty$, but shall be corrected for the influence of other sub-shell configurations, which is larger for ${}^1\Gamma_5$ than for ${}^1\Gamma_4$ with resulting decrease of the distance in the Tanabe-Sugano diagram.

${}^3\Gamma_2-{}^1\Gamma_3$ of $\gamma_5{}^6\gamma_3{}^2$ in d^8. The excited level of the first spin-forbidden band of Ni(II) is intermixed with the triplet levels by intermediate coupling[7,22]. The value of $8B + 2C$ is very little influenced by the other ${}^1\Gamma_3$ from $\gamma_5{}^4\gamma_3{}^4$.

${}^3\Gamma_5(F)-{}^3\Gamma_4(F)$ and ${}^3\Gamma_4(P)$ of d^8. Contrary to the case of Cr(III), all three excited quartet levels can be observed of most Ni(II) complexes, and 15 B thus found form the diagonal sum rule. Further, it has been demonstrated [7,22] that the individual positions of the two ${}^3\Gamma_4$ agree with the theory within some 200 K, (= cm^{-1}) if the deviations from cubic symmetry are not too large.

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[*] When the determinants of d^5 are calculated by use of the rules Ref. [1], p. 173, it is found that most of the non-diagonal elements contain multiples of K-integrals only. The absolute number of J-integrals in each diagonal element is always $n(n-1)/2$ in a d^n-system (because it contains the F^0-integral in the electrostatic case). Thus, the groundstate ${}^6\Gamma_1$ has the energy $J(1.3) - K(1.3) + 3J(1.4) - 3K(1.4) + 3J(3.4) - 3K(3.4) + 3J(4.5) - 3K(4.5)$, while the other states of $\gamma_5{}^3\gamma_3{}^2$ have excitation energies such as ${}^5/_2\, K(1.4) + {}^5/_2\, K(3.4)$ for ${}^4\Gamma_1(G)$, while the energies of ${}^4\Gamma_3(G)$ and ${}^4\Gamma_3(D)$ are a complicated square-root expression in J- and K-integrals, analogous to configurations in gaseous ions, where several multiplet terms present the same LS. The two ${}^4\Gamma_3$ have different parent terms, $({}^4\Gamma_2 . {}^1\Gamma_3)$ and $({}^2\Gamma_3 . {}^3\Gamma_2)$, having as diagonal elements of excitation energy $2K(1.3) + {}^3/_2K(1.4) + {}^3/_2K(3.4)$ and $K(1.4) + K(3.4) + 3K(4.5)$, respectively, but also a non-diagonal element $\sqrt{3}\,(K(1.4) - K(3.4))/2$. The other quartet terms of $\gamma_5{}^3\gamma_3{}^2$ have excitation energies, relative to ${}^6\Gamma_1$, which are the sum of the excitation energies of the parent terms within $\gamma_5{}^3$ (eqn. 14) and $\gamma_3{}^2$ plus a contribution $S'(K(1.4) + K(3.4))$, where $S' = {}^3/_2$ for the quartet-singlet and $S' = 1$ for the doublet-triplet parent terms. It is thus possible to describe the excitation energy within a sub-shell configuration in terms of spin-pairing energy (which can either be a number of K-integrals, or, by the formation of doubly occupied orbitals, differences between J(aa) and J(ab)) and energy due to decreased seniority number v ($v = 0$ for ${}^1\Gamma_1$ of $\gamma_5{}^2$ and $\gamma_3{}^2$, $v = 1$ for ${}^2\Gamma_5$ of $\gamma_5{}^3$).

If the assumption No. 5 on p. 907 of well-defined molecular orbital configurations $\gamma_5^{a}\gamma_3^{b}$, but not necessarily with $l = 2$, is applied to this material, the initial treatment, given by Tanabe and Sugano [5], must be followed. For d-electrons in the octahedral symmetry, a particular theorem is valid:

$$\mathrm{J(aa)} = \mathrm{J(ab)} + 2\ \mathrm{K(ab)} \tag{9}$$

for two different orbitals a and b, which both belong to one of the classes γ_3 or γ_5. Tanabe and Sugano [5] proved that (9) is valid for γ_3, even when it is no d-electron, while (9) is not generally valid for γ_5. Schäffer and the present author have demonstrated from the group-theoretical result, p. 906 that one sufficient condition for (9) is that J(aa) = J(bb) = J(cc) for a, b, c being the irreducible representations in rhombicII. However, this cannot be expected to be valid for all possible γ_5-electrons. The physical significance is the following: if we write the angular function $A = \mathrm{x^a y^b z^c}/\mathrm{r}l$ (with $\mathrm{a} + \mathrm{b} + \mathrm{c} = l$ and $\mathrm{x}^2 + \mathrm{y}^2 + \mathrm{z}^2 = \mathrm{r}^2$) as homogeneous polynomiae in the Cartesian coordinates, the three γ_5-orbitals with $l = 2$ have the three functions xy, xz, and yz. If these functions are rotated 45° in the xy-plane, new linea rcombinations $\sqrt{1/2}\,(\mathrm{xz} + \mathrm{yz})$, and $\sqrt{1/2}\,(\mathrm{xz} - \mathrm{yz})$ are formed with the same physical shape. Analogously, among the p-electrons with $A = \mathrm{x, y, z}$, the linear combination $\sqrt{1/2}\,(\mathrm{x} + \mathrm{y})$ is simply a new p-orbital, only rotated in space. However, for any new such combination $\mathrm{c} = \sqrt{1/2}\,(\mathrm{a} + \mathrm{b})$, where J(aa) = J(bb) and ab having another Γ_n than Γ_1 of a^2 and b^2 (*cf.* the foot-note p. 905), it will be valid

$$\mathrm{J(cc)} = \tfrac{1}{4}\,\{\mathrm{J(aa)} + \mathrm{J(bb)} + 2\mathrm{J(ab)} + 4\mathrm{K(ab)}\} \tag{10}$$

giving (9) if J(cc) = J(aa). This will obviously be the case, if c has the same physical shape as a, only rotated in space. Therefore, Slater's rules mentioned below will be valid for γ_4(p-) and γ_5(d-) electrons, but not for any set of such three equivalent orbitals. Further, by rotation of the xy-orbital, belonging to γ_5, the $(\mathrm{x}^2 - \mathrm{y}^2)$ orbital of γ_3-symmetry can be obtained. Since $(\mathrm{z}^2 - \tfrac{1}{2}\mathrm{x}^2 - \tfrac{1}{2}\mathrm{y}^2)$ can be shown to be equivalent with $(\mathrm{x}^2 - \mathrm{y}^2)$ also in this respect, the J-integrals between two electrons in the same of the five d-orbitals are always identical. In the cases, where (9) is valid, it follows that $^1\Gamma_3$ and $^1\Gamma_5$ of γ_5^2 have the same energy, and that $^2\Gamma_3$ and $^2\Gamma_4$ of γ_5^3 also are systematically degenerate.

It is not easy to compare the molecular orbital theory with experiments, since the interelectronic repulsion energies in the pure sub-shell configurations are described by nine rather than two parameters (the coefficients to the constant $A = F^{\circ} - F^4$, and to B and C in approximation No. 3 are indicated below), *viz*:

$$\begin{array}{ll}
\mathrm{J\ (1.3)} \sim \mathrm{A} - 4\mathrm{B} + \mathrm{C} & \mathrm{K\ (1.3)} \sim 4\mathrm{B} + \mathrm{C} \\
\mathrm{J\ (4.5)} \sim \mathrm{A} - 2\mathrm{B} + \mathrm{C} & \mathrm{K\ (4.5)} \sim 3\mathrm{B} + \mathrm{C} \\
\mathrm{J\ (1.4)} \sim \mathrm{A} - 4\mathrm{B} + \mathrm{C} & \mathrm{K\ (1.4)} \sim 4\mathrm{B} + \mathrm{C} \\
\mathrm{J\ (3.4)} \sim \mathrm{A} + 4\mathrm{B} + \mathrm{C} & \mathrm{K\ (3.4)} \sim \mathrm{C} \\
\mathrm{J\ (4.4)} \sim \mathrm{A} + 4\mathrm{B} + 3\mathrm{C} &
\end{array} \tag{11}$$

since J (1.1) = J (3.3) can be found from eqn. 9, and J (4.4) = J (5, same 5). The numbers denote the tetragonal quantum numbers [3,16]. An interesting theorem is that

$$\begin{aligned} J\,(1.5) &= \frac{1}{4}\,J\,(1.4) + \frac{3}{4}\,J\,(3.4) \sim A + 2B + C \\ J\,(3.5) &= \frac{3}{4}\,J\,(1.4) + \frac{1}{4}\,J\,(3.4) \sim A - 2B + C \\ K\,(1.5) &= \frac{1}{4}\,K\,(1.4) + \frac{3}{4}\,K\,(3.4) \sim B + C \\ K\,(3.5) &= \frac{3}{4}\,K\,(1.4) + \frac{1}{4}\,K\,(3.4) \sim 3B + C \end{aligned} \qquad (12)$$

where 5 denotes one of the two γ_{t5}-orbitals. Thus, the interaction of a filled $\gamma_5{}^6$-shell containing four t5 and two t4-electrons is identical with a t1- or a t3-orbital.

The eigenvalues in the sub-shell configuration $\gamma_5{}^2$

$$\begin{aligned} {}^3\Gamma_4&: \quad J\,(4.5) - K\,(4.5) \\ {}^1\Gamma_5&: \quad J\,(4.5) + K\,(4.5) \\ {}^1\Gamma_3&: \quad J\,(4.4) - K\,(4.5) \\ {}^1\Gamma_1&: \quad J\,(4.4) + 2K\,(4.5) \end{aligned} \qquad (13)$$

can be found from the determinants with identical M_S and a given rhombic Γ_n, giving, *e.g.*, the result that ${}^1\Gamma_1$ the two states of ${}^1\Gamma_3$ are members of a Heisenberg-determinant (p. 905) with the eigen-values J (4.4) + 2 K (4.4) and J (4.4) − K (4.4) twice. With a similar application of one of the two sets of rhombic quantum numbers, the eigen-values in $\gamma_5{}^3$ are:

$$\begin{aligned} {}^4\Gamma_2&: \quad 3\,J\,(4.5) - 3\,K\,(4.5) \\ {}^2\Gamma_3&: \quad 3\,J\,(4.5) \\ {}^2\Gamma_4&: \quad 2\,J\,(4.5) + J\,(4.4) - 2\,K\,(4.5) \\ {}^2\Gamma_5&: \quad 2\,J\,(4.5) + J\,(4.4) \end{aligned} \qquad (14)$$

proving the degeneracy of ${}^2\Gamma_3$ and ${}^2\Gamma_4$ and the ratio 3:5 between the wavenumbers of the first and the third ruby line for γ_5-orbitals satisfying eqn. 9. In the mixed configuration $\gamma_5\gamma_3$, the four energy levels are:

$$\begin{aligned} {}^3\Gamma_5&: \quad J\,(1.4) - K\,(1.4) \\ {}^3\Gamma_4&: \quad J\,(3.4) - K\,(3.4) \\ {}^1\Gamma_5&: \quad J\,(1.4) + K\,(1.4) \\ {}^1\Gamma_4&: \quad J\,(3.4) + K\,(3.4) \end{aligned} \qquad (15)$$

while the quartet levels of $\gamma_5{}^2\gamma_3$ and $\gamma_5\gamma_3{}^2$ have the energies of interelectronic repulsion:

$$^4\Gamma_5(\gamma_5{}^2\gamma_3)\text{: } 3/2\ \mathrm{J}\ (1.4) - 3/2\ \mathrm{K}\ (1.4) + 1/2\ \mathrm{J}\ (3.4) - 1/2\ \mathrm{K}\ (3.4) + \mathrm{J}\ (4.5) - \mathrm{K}\ (4.5) \tag{16}$$

$$^4\Gamma_4(\gamma_5{}^2\gamma_3)\text{: } 1/2\ \mathrm{J}\ (1.4) - 1/2\ \mathrm{K}\ (1.4) + 3/2\ \mathrm{J}\ (3.4) - 3/2\ \mathrm{K}\ (3.4) + \mathrm{J}\ (4.5) - \mathrm{K}\ (4.5)$$

$$^4\Gamma_4(\gamma_5\gamma_3{}^2)\text{: } \mathrm{J}\ (1.3) - \mathrm{K}\ (1.3) + \mathrm{J}\ (1.4) - \mathrm{K}\ (1.4) + \mathrm{J}\ (3.4) - \mathrm{K}\ (3.4)$$

Schäffer and the present author [23] shall discuss, why the structure of all the sub-shell configurations, containing a Γ_4 and a Γ_5 level with maximum value of S, is similar to that of (15) and (16). Thus, the distance between the two spin-allowed bands in d^2-, d^3-, d^7-, and d^8-systems with the symmetry O_h, which is 12 B under assumption of $l = 2$ and an arbitrary radial function, will be:

$$\mathrm{J}\ (3.4) - \mathrm{K}\ (3.4) - \mathrm{J}\ (1.4) + \mathrm{K}\ (1.4) \tag{17}$$

In the special case of diamagnetic d^6-complexes the energy difference ($= 16\ B$ for $l = 2$) between $^1\Gamma_4$ and $^1\Gamma_5$ of $\gamma_5{}^5\gamma_3$ is not given by (17) but by

$$\mathrm{J}\ (3.4) - 2\ \mathrm{K}\ (3.4) - \mathrm{J}\ (1.4) + 2\ \mathrm{K}\ (1.4) \tag{18}$$

and the energy difference between the analogous triplet terms $^3\Gamma_4$ and $^3\Gamma_4$ is only J (3.4) — J (1.4). This can be explained by the interaction with the $\gamma_{t5}{}^4$ core in the five pure tetragonal sub-shell configurations:

t5	t4	t3	t1			
4	2	0	0	$^1\Gamma_1$(t1)	$12\ \mathrm{J}\ (4.5) + 3\ \mathrm{J}\ (4.4) - 6\ \mathrm{K}\ (4.5)$	(19)
4	1	1	0	$^3\Gamma_4$(t2)	$8\ \mathrm{J}\ (4.5) + 2\ \mathrm{J}\ (4.4) - 4\ \mathrm{K}\ (4.5) + 3\ \mathrm{J}\ (1.4) + 2\ \mathrm{J}\ (3.4) - {}^3/_2\ \mathrm{K}\ (1.4) - {}^3/_2\ \mathrm{K}\ (3.4)$	
4	1	1	0	$^1\Gamma_4$(t2)	$8\ \mathrm{J}\ (4.5) + 2\ \mathrm{J}\ (4.4) - 4\ \mathrm{K}\ (4.5) + 3\ \mathrm{J}\ (1.4) + 2\ \mathrm{J}\ (3.4) - {}^3/_2\ \mathrm{K}\ (1.4) + {}^1/_2\ \mathrm{K}\ (3.4)$	
4	1	0	1	$^3\Gamma_5$(t4)	$8\ \mathrm{J}\ (4.5) + 2\ \mathrm{J}\ (4.4) - 4\ \mathrm{K}\ (4.5) + 2\ \mathrm{J}\ (1.4) + 3\ \mathrm{J}\ (3.4) - {}^3/_2\ \mathrm{K}\ (1.4) - {}^3/_2\ \mathrm{K}\ (3.4)$	
4	1	0	1	$^1\Gamma_5$(t4)	$8\ \mathrm{J}\ (4.5) + 2\ \mathrm{J}\ (4.4) - 4\ \mathrm{K}\ (4.5) + 2\ \mathrm{J}\ (1.4) + 3\ \mathrm{J}\ (3.4) + {}^1/_2\ \mathrm{K}\ (1.4) - {}^3/_2\ \mathrm{K}\ (3.4)$	

The two tetragonal sub-shell configurations (3 2 1 0) and (3 2 0 1) do not correspond to pure cubic quantum numbers, Γ_n but have energies, which are

$$\frac{1}{4}\ (\Gamma_4) + \frac{3}{4}\ (\Gamma_4) \text{ and } \frac{3}{4}\ (\Gamma_4) + \frac{1}{4}\ (\Gamma_5) \tag{20}$$

according to eqn. 11. This behaviour of the two levels Γ_{t5} is a general feature for all the sub-shell configurations discussed by Schäffer and the present author [23].

In nickel(II) complexes, the spin-forbidden transitions from $^3\Gamma_2$ to $^1\Gamma_3$ and $^1\Gamma_1$ of the ground configuration $\gamma_5{}^6\gamma_3{}^2$ should have the ratio 1:2 between the wavenumbers, because the excitation energies are those calculated [5] for $\gamma_3{}^2$, *viz.* 2 K (1.3) and 4 K (1.3). It is interesting that the promotion energy forming a planar, diamagnetic complex with the pure tetragonal configuration having an empty γ_{t3}-orbital is 3 K (1.3) because in this case, the level $^1\Gamma_{t1}$ is not intermixed with other tetragonal sub-shell configurations. Thus, the promotion energy [16] indicated as $\frac{4}{7}$ (^{1}D) + $\frac{3}{7}$ (^{1}G), *viz.* $8\,B + 2\,C$ or 2 K (1.3), is too low. In Ni^{++}, however, the state ^{1}S does not seem to have as high an energy as predicted by Slater's theory ($22\,B + 7\,C$ above ^{3}F) with the result that $^1\Gamma_1$ has probably lower energy [22] and that the promotion energy for formation of planar complexes is smaller than 3/2 times the first spin-forbidden transition of the corresponding octahedral complex.

Of course, eqns. 12—19 allow a wider range of variability in the energy differences, where $12\,B$ and $16\,B$ now is explained as a sum of two positive and two negative quantities, and the wavenumbers of the spin-forbidden bands are multiples of K-integrals. It is not easily determined, whether the freedom of molecular orbitals without defined l actually is demanded by experimental evidence. The most surprising fact is that even this theory would predict the same type of ratios between the interelectronic repulsion energies as would the electrostatic model. This has two different aspects: on the one hand, it is very promising for the ligand field theory that nearly any assumption about the wavefunctions would lead to the same distribution of the energy levels of the partly filled shell (agreeing to a high accuracy with observations); on the other hand, unfortunately, it is not easy to draw any conclusions about the wavefunctions from the absorption spectra, except that the electrostatic model is disproven by the nephelauxetic series. One type of evidence about the question how good an approximation is $l = 2$, might be delivered by the temperature-independent paramagnetism, which is proportional to matrix elements of L without regard to the spatial extension of the wavefunctions. Ballhausen and Asmussen [24] have found so enormous residual diamagnetisms by application of Van Vleck's high-frequency formula (which rather was expected to yield too small paramagnetism, due to the neglect of other excited levels) that, disregarding the scattering of the calculated material, the agreement would be much better by taking only 40 % of Van Vleck's correction. This may be explained by a similar break-down of $l = 2$ as the change of the radial functions in approximation No. 3, expressed by the decrease of β. Griffith and Orgel [25] have treated the same problem, but though they applied different experimental values they concluded with the "possible quenching of L", suggesting a similar necessity of molecular orbitals, which are not d-electrons to a very large extent.

However, the success of the ligand field theory seems indirectly to prove that the last of the six approximations, p. 907, the strong intermixing of molecular orbital configurations, is at least not needed for explaining the energy levels. The calculations of this intermixing would be extremely complicated, but of course, it cannot be excluded that the final results would still resemble the observed energy levels. The problem is here common to atomic spectroscopy of gaseous ions: it is not easily proven that the configurations are very pure. However, the magnitude of the correction $\alpha L(L + 1)$ with $\alpha \sim 100$ K, which Trees [26] and Racah [27] introduced to the Slater theory [1] seems to indicate that the configurations usually are ~ 99 % pure in the squares of the wavefunction. It is clearly proven, *e.g.* by Furlani's calculation [28] for Fe^{++}, that the correction due to configuration interaction is monotonically increasing with L. However, the present author has the impression that the terms of the lowest configurations rather are suppressed by a quantity, proportional to $1/(2\ L + 1)$ or $1/(L + 1)$, as also supported by the calculations of Ufford [29], where the non-diagonal elements between LS-terms of d^3 and d^2s are increasing in the series ^2G, ^2F, and ^2P. If such a proportionality with the constant $\sim 10\ 000$ K can be applied, it would explain, why nearly all terms with $L = 0$ seem anomalously much depressed.

However, the agreement of atomic spectroscopy with Slater's theory [1] and of ligand field transitions with Tanabe and Sugano's theory [1] seems to indicate that the electron configurations in gaseous ions and the molecular orbital configurations in octahedral complexes have a purity of the same order of magnitude, *viz.* between 90 and 99 % in most cases.* This may be connected with the fact that the octahedral complexes (more so than, *e.g.*, the square-planar) are so near to having spherical symmetry that most of the electrostatic repulsion between the electrons in the partly filled shell is a common contribution of central field type to all the energy levels, which are not electron transfer states. The latter concept must now be defined as states, where the population of other orbitals than the partly filled γ_3 and γ_5 is changed, relative to the ground-state, since also the d^n-transitions from the old electrostatic model now must be assumed to involve change of the electron density in the ligands. It is a special case of the relatively high purity of molecular orbital configurations in complexes that the number a + b of electrons in the partly filled sub-shells $\gamma_5{}^a\gamma_3{}^b$ still is very good for classification of the complexes according to the oxidation state of the central ion, as implied from the primitive idea of a + b electrons in the d-shell. The classification after d^n may be expected to break down in strongly coloured polymeric complexes of the molybdenum(V,VI) blue or ferro-ferricyanide type, where the partly filled orbitals may be highly de-localized.

It is generally believed that the properties of atoms and molecules are functions of integers (especially the number of electrons) and that these functions are characterized by shell structure, *i.e.* the properties change suddenly by passing certain stabilized numbers. The periodical system of elements is

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* We must here distinguish between the validity of pure configurations in the weak or in the strong sense. In the former, the observed energy differences can be brought in agreement with Slater's theory [1], assuming reasonable values of the parameters of interelectronic repulsion, while the parameters are directly calculated from the radial functions, assuming eqn. 1, in the latter case. Dr. Per Olov Löwdin and Dr. Klaus Appel, Kvantkemiska Gruppen, Uppsala University, have kindly informed me that the interelectronic repulsion invariably is calculated 10—40 % too large in gaseous d^n-ions, showing a rather large deviation from the "strong sense" theory. Thus, we must expect the configuration interaction, introduced by the electronic correlation, to have a similar extent in the transition group complexes [39].

strongly dominated by the stability of 2, 10, 18, 36, 54, 86, . . .electrons, while the nuclei with 2, 6, 8, 14, 20, 28, 40, 50, 82, 126, . . .neutrons or protons are especially stable, as explained by the action of Pauli's exclusion principle on another set of quantum numbers than those of the electrons. It must be realized that these shell structures are entirely dependent on the occurrence of quite pure configurations. In the nuclei, the central field seems strongly apt to deviations from spherical symmetry, and the configurations seem rather intermixed [31,32].

In complexes, it could not be assumed *a priori* that any electron configuration was a good approximation to the wavefunction. Since the time of Sidgwick, it has often been stated that since $S = 0$ of the groundstate of $Co(NH_3)_6^{+++}$, its configuration is to a certain approximation $[A]3d^{10}4s^24p^6$, *i.e.* [Kr], rather than [A] $3d^6$, which would give $S = 2$ and thus a paramagnetic complex. Pauling refined this idea in his hybridization theory, which is actually a molecular orbital theory with assumption of equal radial functions for the d-, s-, and p-part of d^2sp^3. Pauling [33] recognizes that the actual groundstate of most complexes is a resonance structure, *i.e.* an intermixing, of ionic and covalent formulae, and that the magnetic criterion cannot be used for an absolute distinction. However, just the assumption of identical radial functions makes a consistent refinement of this theory very difficult. It was not realized by many authors, that even though the configuration $[A]3d^{10}4s^24p^6$ might be a good description,* i.e. corresponding to the hydrogen-like angular functions for given l, the radial functions may vary from one complex to another, just as they do in the gaseous ions. When the excited states attracted more interest, it was necessary to abandon the valency-bond method for the more general molecular orbital theory. Here, other authors do not recognize that the bonding γ_3- and γ_5-orbitals always are filled, whatever the degree of partly covalent bonding may be, while the total number of electrons in the partly filled shell, represented by the anti-bonding γ_3- and γ_5-orbitals, is constant to a very high approximation. The evolution of partly covalent bonding, as expressed by the nephelauxetic series, corresponds to these anti-bonding orbitals smoothly varying from the d-shell of the gaseous ion to more expanded wavefunctions also present in the ligands. During this development, they may or may not retain $l = 2$ (approximation Nos. 3 and 4) with expanded radial functions, and they do not seem to reach the Pauling value with 50 % participation from the central ion and the ligands, since β still is above 0.3.

The conclusion of this paper is that the assumption (No. 5, p. 907) of negligible intermixing between the configurations $\gamma_5^a\gamma_3^b$ and other molecular orbital configurations seems to be consistent with all facts known about the energy levels and the corresponding wavefunctions. However, the electrostatic model has given a rather fine description, except of the absolute value of Δ (but it must now be rejected due to the nephelauxetic effect) so it cannot easily be concluded conversely that satisfactory agreement has proven the

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* However, corresponding to spherical symmetry of the electron cloud. Only after having formed the covalent bonds, the hybridized configurations have any directional character, as not always recognized.

validity of the approximation of pure molecular orbital configurations of the partly filled shell, which is rather near to being a d-shell.

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