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RECENT THEORETICAL DEVELOPMENTS IN PHOTOCHEMISTRY

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Between, say 72 and 82, much of the photosubstitution chemistry of trivalent chromium, cobalt, rhodium and iridium-compounds was rationalized in terms of ligand field theory [1,2,3]. Whether one is convinced by these rationalizations or not, depends on a number of things, for instance on whether one believes that the photosubstitution reactions are dissociative rather than associative. But this is not a point that we will discuss at length in this review. We rather want to focus on the methodology of the ligand field approach as such. More specifically, we would like to address the problem of the underlying physical and chemical assumptions of ligand field theory. We will do so by comparing certain ligand field results with a number of *ab initio* calculations relevant to spectroscopy and photochemistry. Indeed, it is a fact that *ab initio* calculations are becoming more and more feasible, not only for individual transition metal compounds, but also for the analysis of photochemical reaction paths.

And since by definition, we do not make any a priori assumptions if we carry out *ab initio* calculations, it should be possible to examine the physical soundness of the ligand field premises.

LIGAND FIELD VERSUS AB INITIO PREMISES

Let us recall very briefly what we consider to be the most important and basic ligand field premises [4,5] : the valence orbitals are supposed to be the highest occupied molecular orbital and to consist essentially of nearly pure metal d-orbitals; the ligand orbitals are supposed to be fully occupied and lower in energy. The ligand field is assumed to be describable in terms of perturbation theory, and the total ligand field perturbation as a simple sum of individual ligand perturbations, leading to the well-

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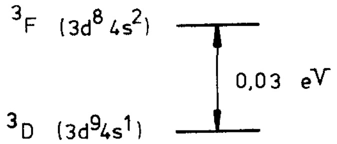
known additivity and transferability properties of ligand field theory. The one-electron orbital energy difference is expressed in terms of σ and π parameters, the repulsion by the Racah B and C parameters. For octahedral complexes, the balance between 10Dq and the spin-pairing energy P is supposed to determine the high-spin or the low-spin character of the ground state.

Now, what can we expect if we carry out *ab initio* calculations on these very same systems ? Let us consider three examples of statements that have been made in the past on the basis of *ab initio* work :

1. One of the earliest calculations reported a negative value of 10Dq for an octahedron : the valence electrons were computed to be more attracted to the ligand nuclei than they were repelled by the ligand electrons. This conclusion was not due to a logical error, but turned out to be the consequence of the rather crude approximations one had to make in the evaluation of the integrals. Present day calculations always lead to the expected sign of the spectrochemical parameter. But the reason why we mention this early result is that it illustrates in a rather convincing way that an *ab initio* calculation definitely questions everything.
2. More recently, it has become fashionable to claim that Hartree-Fock theory is essentially useless for transition-metals and transition-metal compounds. Indeed, Hartree-Fock theory is said to be unable to predict even the correct ground state of the Ni-atom, and therefore, *ab initio* work on transition-metals is claimed to be only meaningful if it goes beyond the Hartree-Fock level and if it incorporates a significant part of the correlation energy.

   And indeed, Hartree-Fock calculations predict a d^8s^2 ground state whereas the experimental ground state corresponds to d^9s^1. However, ΔE is only a few hundreds of an eV, and Ni is the only first-row transition-metal atom, where the ground state is not correctely predicted at the Hartree-Fock level. Therefore, it seems somewhat exaggerated to reject Hartree-Fock so radically, at least for qualitative purposes. There is no need to stress that the same circles that criticize Hartree-Fock calculations, are not very impressed by ligand field theory either. We will not



adopt this point of view, but we have to be aware of the fact that even today obtaining quantitative agreement with experiment remains a very tough job in the field of transition-metal chemistry.

3. A third statement that we would like to comment upon briefly has to do with the multiplet-splitting of a given configuration. Consider the d^8 configuration of the Ni(II)-ion. According to the conventional Slater-Condon-Shortley theory, the resulting multiplets have a different energy because they correspond to different occupations of the five degenerate d-orbitals exhibiting different spin orientations, and therefore different interelectronic repulsions. The conventional multiplet theory predicts that ^3F is the ground state because it has the lowest interelectronic repulsion, as described by the Racah parameters B and C. Both Hartree-Fock calculations and more advanced, nearly exact calculations show on the contrary that ^3F carries the largest interelectronic repulsion ($E = E_1 + E_2$: one- and two-electron contributions to the energy). The sequence of the two-electron energies E_2 is exactly opposite from what conventional multiplet theory expects, and the rationale for the total energy sequence has to be found in the evolution of E_1, more specifically in the evolution of the electron nucleus attraction terms [6,7].

   The rationalization of this phenomenon can readily be found by realizing that conventional multiplet theory is just a straightforward application of first- and second-order perturbation theory. Now, first-order perturbation theory is incompatible with the virial theorem, requiring $E = -T$. Indeed, if the different multiplets are described by the same set of orbitals – which is the usual approach of perturbation theory – all states are predicted to have the same kinetic energy T, and the same one-electron energy E_1. But then, from the virial theorem, they could not possibly have a different repulsion energy. What actually would happen if one started off from the ^3F Hartree-Fock ground state and if one uses these very same orbitals to construct one of the other multiplet functions, is that one forces an undue amount of repulsion into this wavefunction. Therefore the function and especially the d orbitals are going to expand so as to reduce the unnatural amount of repulsion. The wavefunction is said to relax to its ground shape. If a wavefunction expands, also the one-electron part of the energy changes, and the expansion stops when the virial theorem is satisfied again. When this new equilibrium is reached, it is found that the total relaxation energy is very small, but that the components have changed very much. Actually, it turns out that the two-electron repulsion E_2, which was larger for the excited states (if one uses perturbation theory) now becomes smaller in the excited states than in the ground states. So, the expansion entails an over-compensation of the originally imposed change in two-electron repulsion energy. Obviously, these observations suggest that we reconsider the physical meaning of the Racah parameters B and C, which were supposed to be pure two-electron repulsion parameters. Apparently, in some cases, *ab initio* calculations are able to throw new light on old parameters. This result seems to be of particular relevance in the transition from high-spin to low-spin complexes, which is supposed to depend on the relative magnitude of the one-electron parameters versus the two-electron parameters.

So, as a conclusion of these considerations, what can we expect from *ab initio* calculations for transition-metal complexes ? Everything depends on the level of sophistication, at which the calculations are performed. If the calculations are too crude, the results can be qualitatively meaningless and very misleading as in the first example. If we carry out Hartree-Fock calculations, with a large basis set (possibly with a limited configuration interaction within the d^n-configuration), the results should in general at least be qualitatively satisfactory. This is the level of sophistication that is probably best suited to make a comparison with ligand field models, and to find out whether or not the conceptual framework of ligand field analysis is adequate. For instance, in the third example given above, the unusual variation of the interelectron repulsion is clearly apparent already at the Hartree-Fock level.

Therefore, in the rest of this review, we will focus on this intermediate level of sophistication.

But before doing so, just for the sake of comparison, it may be useful to show the result of the different methodologies in one example (See Table I). This Table compares the experimental spectral data for the Chromium(III) hexafluoride cluster with the Hartree-Fock results and with the results of partially correlated wavefunctions that we have carried out quite recently [8]. As for the quartet-quartet transitions, corresponding to t_{2g} versus e_g transitions, the Hartree-Fock calculations are not unsatisfactory; for many other compounds, the SCF results are definitely worse; in general 10Dq tends to be calculated too low. For the specific example here, we are apparently rather lucky at the SCF level. The doublet states are much worse; they all correspond to the same $t_{2g}{}^3$ configuration as the ground state, and they are calculated much too high. This illustrates a well-known deficiency of Hartree-Fock theory : one often gets poor results if one compares states with different multiplicity. Indeed, in the quartet states, the Pauli correlation keeps the three electrons with parallel spin away from each other already at the Hartree-Fock level, whereas the doublet wavefunctions lack the corresponding Pauli correlation.

Table I

Comparison of *ab initio* results with experimental data for CrF$_6^{3-}$ (energies in cm^{-1}) [Taken from ref 8]

CrF$_6^{3-}$ (energies in cm^{-1})

	State	Expt	Hartree-Fock	Correlated
t_{2g}^3	$^4A_{2g}$	0	0	0
$t_{2g}^2e_g$	$^4T_{2g}$	14900	13790	14330
	$^4T_{1g}$ (a)	22700	26774	22000
	$^4T_{1g}$ (b)	34400	30408	34850
t_{2g}^3	^2E_g	15700	22070	17470
	$^2T_{1g}$	16400	22050	18680
	$^2T_{2g}$	22000	36433	22440

In the last column, the results are improved rather significantly, and for nearly all states, we come close enough to experiment to call the agreement quantitative. Indeed, the influence of the second coordination sphere or of the crystal environment induces energy shifts of the order of 1000 cm^{-1}, which is hardly less than the difference between theory and experiment.

It must be stressed though that the incorporation of electron correlation in systems of this size is not a trivial matter. These are expensive and time-consuming calculations of the multiconfiguration SCF type, followed by a multireference configuration interaction. For some of these states, nearly half a million configurations were included. Now, this is what we need, if we want quantitative agreement with experiment, that is if we want an accuracy allowing unambiguous spectral assignments. But this may not what we need, if we want to look at the validity of the basic assumptions of ligand field theory. In that case, we prefer to stop at the Hartree-Fock level, or just a small step further towards correlated wavefunctions, by incorporating a very limited configuration interaction within the d^n states, exactly as it is done in ligand field theory.

THE VALENCE SHELL IN TRANSITION METAL COMPLEXES

If we do so, what are some of the most important conclusions ? We will cite from our own work, as well as from the work of other theoretical groups [9-13]. The first conclusion, that is perhaps most widely known already, is that the general orbital pattern from SCF theory can be said to confirm the ligand field ideas : the open-shell valence orbitals are slightly antibonding and they are predominantly d orbitals on the metal. As a matter of fact, the molecular $\tilde{d}\sigma$-orbitals are something like 85 % or 90 % pure d orbitals, whereas the $\tilde{d}\pi$-orbitals are generally, say 97 to 99 % pure d orbitals. Analysis of overlap populations clearly shows that the d orbitals play a substantial role in the bonding of the ligand [14]. Hence it should not be surprising that a $\tilde{d}\pi \longrightarrow \tilde{d}\sigma$ excitation has a pronounced effect on the M-L bond strengths. This view of the coordination bond effectively opposes the assertions of Gerloch and Woolley [15], claiming that the primary bond formation occurs between the ligand orbitals and the 4s and 4p functions of the metal valence shell. It is true though that the 4s and 4p orbitals do play a certain role in the corresponding bonding orbitals; but their contribution remains always smaller than the contribution of the d orbitals.

Before leaving this point, we have to stress that the incorporation of correlation in general increases the covalency of the metal-ligand bond. Figure 1 shows a total density difference plot for CrF_6^{3-}; more specifically it shows the difference between the correlated density and the Hartree-Fock density, and one sees very clearly how electrons flow from the ligands (dashed contours) to the metal (full contours). Indeed, it is a well-known [9,16] deficiency of Hartree-Fock that it underestimates somewhat the covalency of the metal-ligand bond. But still, even in the framework of a correlated calculation, the quantitative implications of this density shift do not modify the picture of a very ionic bond, where the d orbitals play a predominant role.

A second conclusion that follows from the *ab initio* calculations is that the metal orbitals are not – in general – the frontier orbitals, as assumed by ligand field theory, but nevertheless, the first excited states are invariably found to be dd transitions. The reason is that the repulsion between two electrons in an (essentially localized) $\tilde{d}$ orbital ($\tilde{d}\tilde{d}$), is much larger than the repulsion between two electrons in a (very delocalized) $\tilde{l}$ orbital, which is spread out over the whole molecule. Therefore $(\tilde{d},\tilde{d}) > (\tilde{l},\tilde{l})$ and $(\tilde{d},\tilde{l})$ has intermediate values. Consequently, it would require energy to drop an electron from the highest occupied molecular orbital into the lower lying $\tilde{d}\pi$ orbitals; metal to ligand charge transfer states have in general a high energy. It would also require much energy to take an electron from the highest occupied molecular orbital into $\tilde{d}\sigma$, a good deal more than to take an electron from $\tilde{d}\pi$ to $\tilde{d}\sigma$, because in the first case, which is a ligand to metal charge transfer one replaces an $\tilde{l}\tilde{l}$ repulsion by a $\tilde{d}\tilde{d}$ repulsion, whereas in the second case, one stays within the d^n states, and one does not change the nature of interelectronic repulsions.

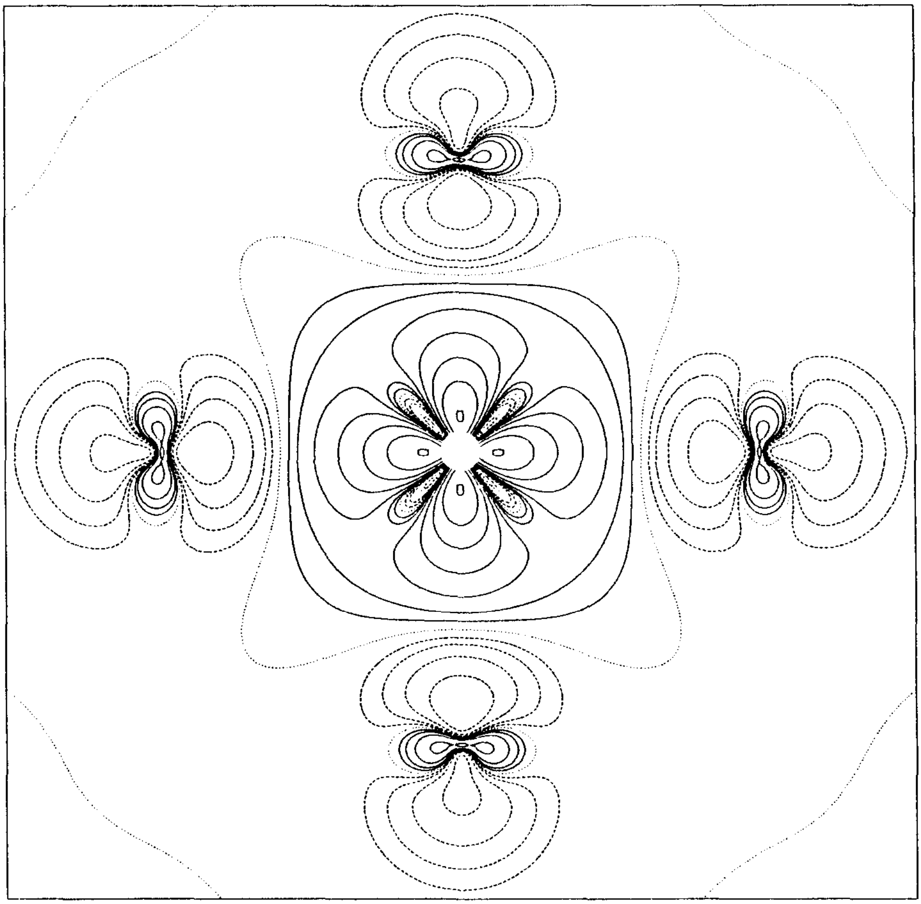


Figure 1. Total density difference plot (in one coordinate plane) for the ground-state of CrF_6^{3-}, showing the effect of correlation : $\Delta\rho = \rho_{\mathrm{corr}} - \rho_{\mathrm{HF}}$. Full contours correspond to an increase in electron density and dashed contours to a decrease in electron density. At the dotted lines $\Delta\rho = 0$

The situation is comparable, to some extent, to the configurational problem of the neutral transition-metal atoms, where the ground state configuration always contains one or two 4s electrons. Here as well, the much larger size of 4s with respect to 3d, entails the inequalities (dd) > (ds) > (ss). Therefore, dropping an electron from 4s to 3d increases the interelectronic repulsion to such an extent that the result is an excited state [17].

The third conclusion has to do with the additivity and the transferability properties of ligand field theory. The most straightforward way to study this phenomenon is to carry out a number of *ab initio* calculations on substituted complexes. In Figure 2, we see the orbital energy η of the $\tilde{d}$-orbitals in five chromium(III) complexes, the octahedral $Cr(NH_3)_6^{3+}$, and a number of mono- and di-substituted Chromium-ammines. The remarkable point is that these *ab initio* results apparently satisfy – in a nearly perfect way – the relationships that one would expect on the basis of additive ligand perturbations, operating on pure metal orbitals. In the case of the cis-complex for instance, the relevant symmetry of the perturbation is the holohedron symmetry [5], which is D_{4h}. In the present *ab initio* calculation, the actual symmetry was only C_{2v}, and the fact that the effective symmetry turns out to be higher – although this was not imposed a priori – is a rather striking indication of the

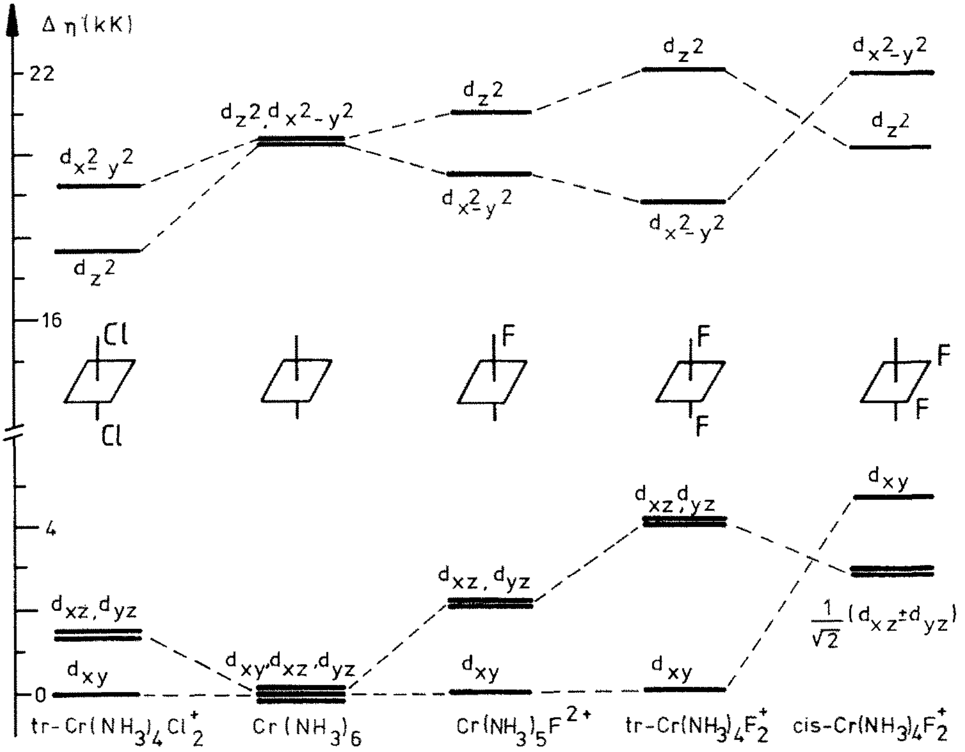


Figure 2. Relative orbital energies (η) in overall substituted chromium(III) ammines [Taken from ref 14].

validity of the additivity postulate. This result is of course directly related to the fact that the 3d orbitals do (virtually) not mix with 4s or 4p orbitals, although there are no symmetry reasons preventing them from doing so in a C_{2v} environment. Furthermore, the energy diagram also shows that the interaction of the individual ligands with the metal are essentially simply additive. The same conclusion is also apparent from an analysis of the trans-complexes : both for the σ and the π orbitals, the energy splittings of the trans-complex are very close to twice the energy splittings of the mono-substituted complex. We have a sign inversion from cis to trans, and the cis splittings are about equal to the splittings of the mono-substituted complex. The corresponding state energies for these complexes also exhibit the same type of regularities.

Similar results were obtained for mono- and dihydroxo-substituted complexes of Co(III) hexacyanide. Therefore, it seems reasonable to conclude that the *ab initio* results support the idea of ligand additivity and transferability. Again, this conclusion seems to disagree with the point of view of Gerloch and Woolley [15], who suggest that ligand replacements should give rise to rather extensive charge redistributions in the complex, affecting the bonding properties of the other ligands. They suggest that these charge redistributions should be governed by Pauling's electroneutrality principle [18]. Now, if we look at the Hartree-Fock charge densities, we do observe certain small shifts upon substitution. These shifts can in general be rationalized quite simply from a charge effect. If a negative ligand, such as F^- or Cl^- replaces a neutral NH_3 ligand, the added negative charge will hinder to some extent electron donation from the other ligands to the metal. The calculated population changes are not insignificant and in that sense, Gerloch and Woolley do have a point, but the corresponding variation of the ligand field parameters is obviously quite small, and the transferability idea cannot be said to be seriously affected.

THE PREDICTION OF LIGAND FIELD PARAMETERS

The next result concerns the *ab initio* prediction of the typical ligand field parameters that have proven to be so successful in describing the spectroscopic properties of transition metal compounds. More specifically, we will look at the spectrochemical parameter 10Dq, the two-dimensional spectrochemical series described by σ and π, the Racah parameters B and C, and the nephelauxetic series described by $\beta = B/B_0$. Table II shows the evolution of 10Dq for three typical octahedral Chromium-compounds : a weak field ligand, an intermediate field and a strong field ligand. The Hartree-Fock calculations reproduce the trend quite faithfully, but

Table II

Hartree-Fock prediction of 10 Dq values (10 Dq = $E(^4T_{2g}) - E(^4A_{2g})$) for three typical Cr(III) complexes

in cm^{-1}	CrF_6^{3-}	$Cr(NH_3)_6^{3+}$	$Cr(CN)_6^{3-}$
10 Dq_{expt}	15370	21540	26700
10 Dq_{HF}	13790	19590	23051

quantitatively, the *ab initio* method yields values, which are systematically somewhat too low in energy. Overall, this represents a pretty good result, but we should stress that the physical picture behind the *ab initio* result is very different from the conventional ligand field picture. In the conventional ligand field picture, the $t_{2g} \rightarrow e_g$ transition of $Cr(III)L_6$ is a pure one-electron transition : the two-electron dd repulsion energy E_2 is supposed to remain unchanged in the process. The higher energy of the e_g orbitals is supposed to be due entirely to the fact that the σ orbitals come closer to the negative ligands, represented by negative point charges, for instance. Therefore, in ligand field theory, 10Dq is a purely one-electron potential energy difference. This is incompatible with the virial theorem and indeed, Hartree-Fock theory reveals a different picture. The positive value of 10Dq turns out to be due essentially (but not exclusively) to an increase in kinetic energy, associated with the stronger antibonding character of the $d\sigma$ orbitals. This result complies with Jørgensen's comment on the role of the kinetic energy as an essential constituent of the spectrochemical parameters [19].

Rather than to go into the details of this analysis, we will take a closer look at the two-dimensional spectrochemical series. From the splitting pattern resulting from the HF calculations on substituted complexes, one can derive "*ab initio* σ and π" values or rather $\Delta\sigma$ and $\Delta\pi$ values. It turns out that the sequence of the parameters is the same as in the semi-empirical work : the F^- ion is both the stronger σ and the stronger π ligand. Cl^- is the weaker σ ligand and ammonia is the weaker π ligand. As a mattter of fact, it is common practice to set $\pi_N = 0$; this can always be done, since only the differences $\Delta\pi$ can be obtained. Now, if we consider the calculated t_{2g} $\tilde{d}_\pi$ orbitals of the octahedral $Cr(NH_3)_6^{3+}$ complex, population analysis reveals more than 99 % pure d orbitals, which is more than for any other complex as far as we know. This observation could be taken as an indication that it is a reasonable choice to set the π parameter of NH_3 equal to zero.

In general however, we have to be careful to make a clear distinction between the mixing of L and M orbitals as revealed by population analysis, and their spectrochemical strength. For instance, if we compare the previously considered mixed fluoro or chloro ammine complexes, population analysis shows that the σ metal-ligand mixing is largest for Cl^- and smallest for F^-. Therefore, the so-called σ donor properties of the ligands vary as $F < NH_3 < Cl$, which is just the opposite sequence as for the spectrochemical strength. The reason is of course that the σ donor properties, or the covalency is more adequately reflected by the nephelauxetic series, which indeed contains these very same inequalities.

Experimentally, the nephelauxetic series is determined from the ratio of the Racah B parameters in the complex and in the free ion. The closest analogue to this β ratio, that can be obtained from an *ab initio* calculation, is the ratio of the average $(\tilde{d},\tilde{d})$ repulsion energy over the atomic (dd) repulsion energy. Table III shows $\tilde{d}\tilde{d}$ for seven different complexes as compared to dd for free atomic chromium. The numbers in the last column are the ab intio equivalent of β. One obtains of course exactly 1 for the atomic ion itself. If we take $Cr(NH_3)_6^{3+}$ as a starting point, one sees that progressive

Table III

Average d,d repulsion between two electrons in d orbitals of Cr^{3+} [from ref. 10-13]

(d,d) = 0.818 Hartree

Complex	$(\tilde{d},\tilde{d})$	$(\tilde{d},\tilde{d})/(d,d)$
CrF_6^{3-}	0.768	0.939
tr-$Cr(NH_3)_4F_2^+$	0.749	0.916
cis-$Cr(NH_3)_4F_2^+$	0.746	0.912
$Cr(NH_3)_5F^{2+}$	0.743	0.909
$Cr(NH_3)_6^{3+}$	0.741	0.906
tr-$Cr(NH_3)_4Cl_2^+$	0.738	0.902
$Cr(CN)_6^{3-}$	0.711	0.869

replacements of NH_3 by F^- increase the ratio, corresponding to a decreasing covalency; in the limit, CrF_6^{3-} is the most ionic complex. Replacement of NH_3 by one Cl^- decreases the ratio, corresponding to increasing covalency. The most covalent complex is $Cr(CN)_6^{3-}$.

So here again, *ab initio* work does confirm a whole set of ligand field ideas. The most striking difference was the physical interpretation of 10Dq. A similar striking difference was revealed by the analysis of the Racah B-parameters, in atomic systems. Something similar can be found in the molecular complexes, and we will discuss this point in more detail in the following set of results, concerning the high-spin ⟷ low-spin transition.

In order to illustrate this point, we selected a d^6 system, where we compare the high-spin CoF_6^{3-} – with a quintet ground state – with the low-spin $Co(CN)_6^{3-}$ complex, with a singlet ground state. The conventional ligand field approach is based on the Tanabe-Sugano diagrams where we have on the one side the zero field situation, that is the free metallic ion, and on the other side the very strong field situation, where the repulsion is negligible. In Figure 3 we show part of such a diagram, but this time calculated within the Hartree-Fock approximation. In the middle, we show the lowest state of each multiplicity in Co^{3+}. At the extreme left and right, we show the configuration averages for CoF_6^{3-} and $Co(CN)_6^{3-}$; in between we show a selection of a number of particularly relevant states. The most striking point is of course that the Hartree-Fock level correctly predicts the ground state in both cases, and the corresponding high-spin ⟷ low-spin transition.

Conceptually, the calculations offer a rather fascinating mixture of confirmations and refutations of the ligand field picture. For instance, as expected, the interconfigurational separations are larger for the strong field complexes, but the energy gaps are not constant, as would be anticipated from ligand field theory; they increase with increasing electron population. Indeed, due to the larger covalency of the $\tilde{d}\sigma$ orbitals, the average repulsion of the electrons in $\tilde{d}\sigma$ is smaller than in the $\tilde{d}\pi$ orbitals. As a consequence, $(e,e) < (e,t_2) < (t_2,t_2)$. This differential covalency is of course completely absent from the ligand field picture, and it turns out to be at the basis of the increasing interconfigurational gaps at the Hartree-Fock level.

If we look at the atomic ion, conventional multiplet theory associates the smaller repulsion to ^5D, the larger repulsion to ^1I, but we have seen already that Hartree-Fock calculations lead us to the opposite result : the atomic quintet carries the largest repulsion. How about the molecular complexes? Here, we have something similar; consider for instance the four states corresponding to the same $t_2^5e^1$ configuration i.e.

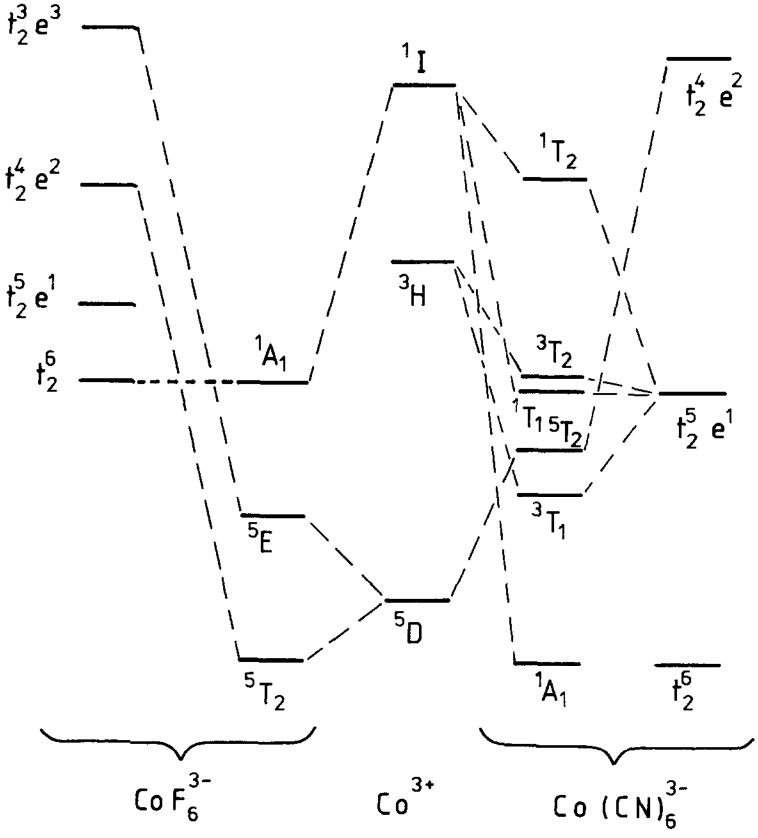


Figure 3. Comparison of energy diagrams for a high-spin and a low-spin Co(III) complex.

$^{1,3}T_1$ and $^{1,3}T_2$. According to conventional ligand field theory, the repulsion would increase from bottom to top, but *ab initio* calculations reveal exactly the opposite trend, for the same reasons as detailed before.

However, when we turn to a comparison of $^1A_1$ and $^5T_2$, in both cases, CoF_6^{3-} and $Co(CN)_6^{3-}$, the conventional predictions are found to be realized, and the molecular singlet states carry the largest repulsion. But the reason why this happens, is completely different from what one could expect. Indeed, the spin pairing is definitely not the reason, as evidenced by the atomic situation and by the the t^5e^1 situation. The actual reason is something that is neglected by ligand field theory : it is again the differential covalency between $\tilde{d}\sigma$ and $\tilde{d}\pi$ orbitals. Indeed, since the $\tilde{d}\pi$ orbitals are much more ionic than the $\tilde{d}\sigma$ orbitals, the former are more localized and they carry the larger repulsion.

So the conclusion appears to be that ligand field theory – like atomic multiplet theory or Hund's rules – is better than the rationale upon which it has been built. The fact that its physical basis can be criticized on the basis of *ab initio* calculations does not prevent it from having an undeniable predictive value.

ANALYSIS OF PHOTOCHEMICAL REACTION PATHS

Let us see in our final point what *ab initio* calculations can learn us in the analysis of photochemical reaction paths. Let us consider one of the typical stereomobile substitution reactions of a Cr complex : if $Cr(NH_3)_5F^{2+}$ is irradiated in its ligand field bands, one obtains a predominant axial ammonia loss, and a secondary equatorial NH_3 loss. The experimental results appear to lead to the conclusion that one has a stereomobility in both cases. If the trans NH_3 is replaced by a water molecule, the reaction product is cis; if the cis NH_3 is replaced by a water molecule, the reaction product is predominantly trans [20-22].

The ligand field rationalization that was proposed to explain these phenomena was based on a five-coordinated intermediate CrN_4F and its different possible isomers and isomerization paths. Figure 4A shows two square pyramids, one with the F atom in apical position and the other one with the F atom in equatorial position, and also two trigonal bipyramids, again with F in equatorial or in axial position. The transition between a square pyramid and a trigonal bipyramid is most simply described by a bending motion of two ligands. The energy levels were calculated by means of ligand field theory and by using semi-empirical σ and π parameters. The proposed sequence runs as follows : in an axial labilization process, the five-coordinated fragment SP_{ap} is generated in its ^4E excited state, that spontaneously rolls down to the TBP_{eq} in its $^4B_2$ ground state and further down to the $^4A'$ ground state of the alternative square pyramid. This structure has one vacant site with an empty d_{z^2} orbital, ready to accept an increasing water ligand so as to yield a cis-reaction product. Similarly, in an equatorial labilization, the five-coordinated fragment is generated in its excited $^4A'$ state and transforms spontaneously into the same TBP_{eq}, but this time in its $^4A_1$ state which is symmetry-connected to the lower lying $^4B_1$ state of SP_{ap}. From there on, water addition generates a trans product.

Parenthetically it should be noted that the correlation diagrams presented in fig. 4 only show one-dimensional sections through the reaction surface. For a more detailed

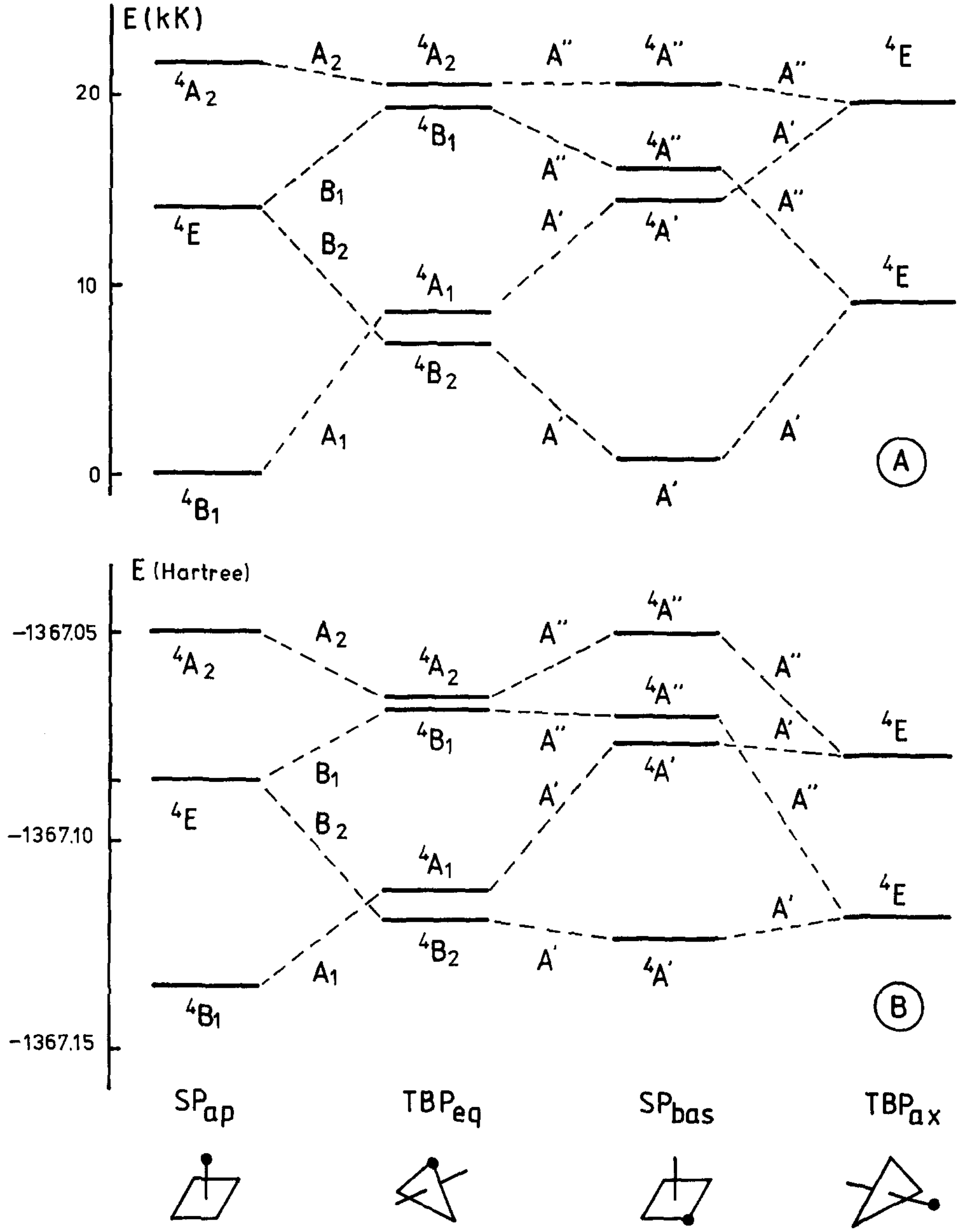


Figure 4A. State correlation diagram for the isomerization of the $Cr(NH_3)_4)F^{2+}$ fragment calculated by ligand field methods; Figure 4B. State correlation diagram for the isomerization of the $Cr(NH_3)_4F^{2+}$ fragment calculated by *ab initio* methods.

picture of the reaction dynamics one should turn to a multi-dimensional representation of the surface. For the present example such a representation can be based on a Jahn-Teller type treatment, as we have shown elsewhere [20,23].

We were curious to find out whether the same kind of diagrams would be supported by initio calculations, which was certainly not obvious a priori, especially considering the important role of the precise relative energies of the different levels, and considering that the five-coordinated intermediates were never observed directly, but were calculated by using the semi-empirical parameters derived from experimental data on hexacoordinated complexes.

Figure 4B shows the result of the *ab initio* analysis, which turns out to be similar to the previous one (Fig. 4A) in a rather astonishing way. The same type of amazingly good agreement between *ab initio* and ligand field calculations was found for the CrN_4Cl fragment, suggesting that simple ligand field calculations are indeed able to rationalize the photochemistry of the Cr complexes.

One observes from Fig. 4 that the difference between axial and equatorial labilization pathways is crucially related to the properties of the $^4A_1$ and $^4B_2$ states of the TBP_{eq}. Figure 5 shows the density difference $\rho(^4A_1) - \rho(^4B_2)$ in the equatorial plane containing twice NH_3 and one F ligand. One sees quite clearly the occupation of the $\tilde{d}_{yz}$ orbital in $^4A_1$ (full lines) and the occupation of the $\tilde{d}_{z^2-y^2}$ orbital in $^4B_2$ (dotted lines), again precisely in agreement with the simple ligand field picture.

However, the final conclusion is not that *ab initio* calculations always reproduce the reaction paths and confirm the reaction mechanism proposed by ligand field theory. It is true that this would seem to be the case on the basis of the few results for Cr(III) complexes.

We are not sure though that these conclusions can be generalized to d^6 systems. As a matter of fact, our preliminary results on Co(III) complexes suggest a number of important deviations and difficulties. Right now, it seems more probable that the relationship between semi-empirical ligand field theories and *ab initio* calculations will turn out just as subtle and delicate for photochemical applications as they were for spectroscopy.

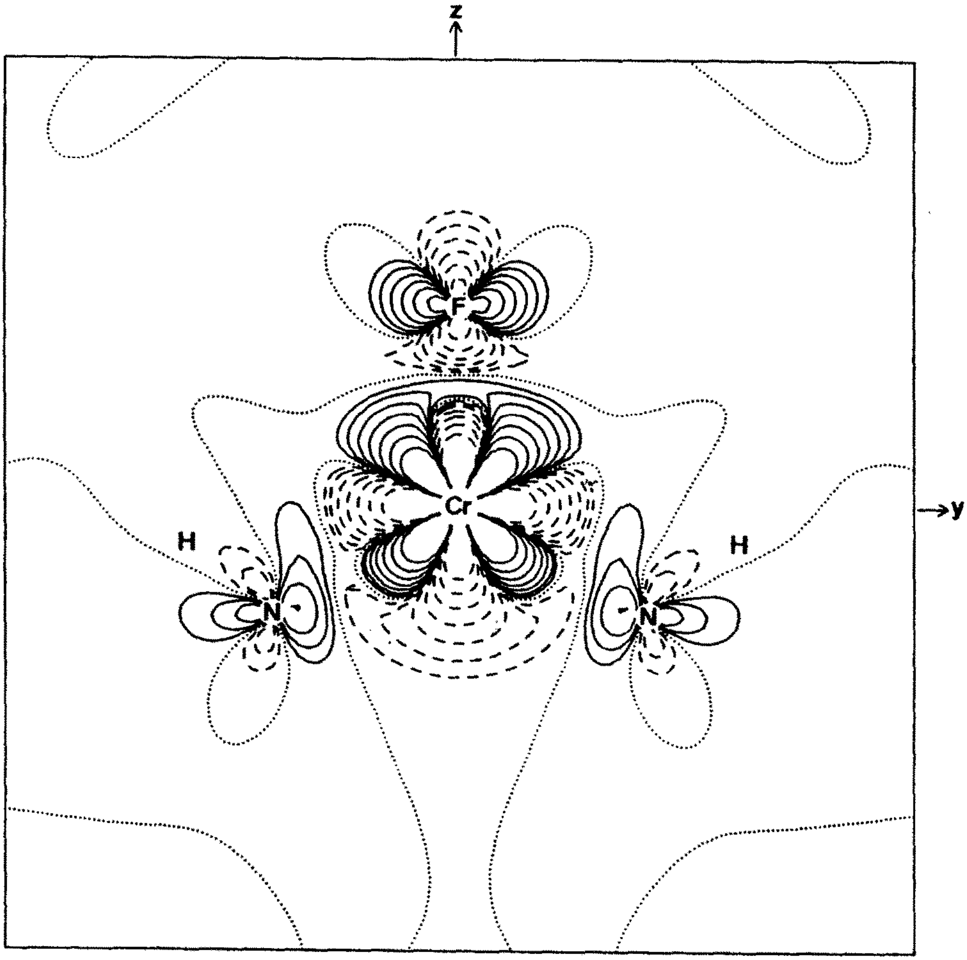


Figure 5. Total density difference plot $\Delta\rho = \rho(^4A_1) - \rho(^4B_2)$ for the equatorial plane of the $Cr(NH_3)_4F^{2+}$ fragment in a TBP_{eq} geometry.

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