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Theoretical Aspects of Transition Metal Chemistry

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Theoretical Aspects of Transition Metal Chemistry

The stereochemistry of transition metal complexes can be properly discussed by means of ligand field theory. It is stressed, however, that the Racah *B* and *C* parameters do not have a simple interpretation in the description of d–d repulsions.

INTRODUCTION

In a sense, ligand field theory has a better status now than it had two decades ago. In the early sixties, everyone realized that the point charge model was physically absurd. For many this was considered a good reason to abandon ligand field theory altogether. As a consequence semiempirical MO theories of the extended Hückel (EHT) or the SCCC type became very fashionable.

At the same time, and in part as a reaction against the justified criticism of the point charge model, Jørgensen and Schäffer[1] developed the angular overlap model (AOM). This model systematized the earlier ideas of Yamatera[2] and McClure[3] on the two-dimensional spectrochemical series. The individual metal–ligand bond is analyzed in σ and π components, depending on the number of nodal planes through the bond. While maintaining the original crystal field formalism, the angular overlap model is chemically appealing and the interpretation of some of its parameters has obvious roots in molecular orbital theory.

Subsequent years witnessed a somewhat parallel application of both extended Hückel and angular overlap theories to a large variety of complexes. AOM appears to be better suited to applications where the open shell d–d repulsion has to be considered explicitly, while EHT might be preferred whenever delocalization effects are important.[4] In

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this Comment we intend to illustrate the use of angular overlap considerations in the study of certain categories of chemical reactions.

SELECTION RULES IN TRANSITION METAL PHOTOCHEMISTRY

The photosubstitutions of both d^3 and d^6 complexes turn out to be remarkably stereospecific: in many cases the ligand replacement in a hexacoordinated complex is either completely stereoretent, or else completely stereomobile.[5–7] Any attempt to understand this behavior has to be based on a well-defined reaction mechanism. In what follows we will adopt a dissociative mechanism for both d^3 and d^6 systems.[8,9] Thereby the reaction is formally divided into two or three consecutive steps: first the hexacoordinated complex loses one ligand and becomes a five-coordinated square pyramid (SP); this SP fragment may or may not rearrange to a trigonal bipyramid (TBP); the final step is the addition of the incoming ligand (or solvent molecule) to either the SP or the TBP to restore hexacoordination.

If this mechanistic hypothesis is correct, the stereochemistry of the reaction is determined by two questions: (i) is the SP–TBP rearrangement possible? (ii) if so, how will the entering ligand attach itself to the five-coordinated molecule?

To answer these questions, let us consider a five-coordinated fragment containing four equal ligands L (such as amine or cyanide) and one weak-field heteroligand X, such as a halide. This situation, depicted in Figure 1, covers many (in fact, most) experimental data. It should be stressed however, that other possibilities *can* arise—for instance, when X has a stronger ligand field than L, or when the five-coordinated fragment contains two heteroligands. For a discussion of these (more intricate) cases, we refer to the literature.[10–13] The present Comment will be confined to the simple situation shown in Figure 1.

In principle, both square pyramids I and II can give rise to two different trigonal bipyramids: A (equatorial heteroligand) and B (axial heteroligand). *When the molecule (d^3 or d^6 complex) is in its first excited photoactive state, B is inaccessible along both distortion paths; A on the contrary is accessible and can be obtained from either SP.*

In order to verify this conclusion, Figure 2 shows the two distortion possibilities of the square pyramid I. The symmetry conserved along

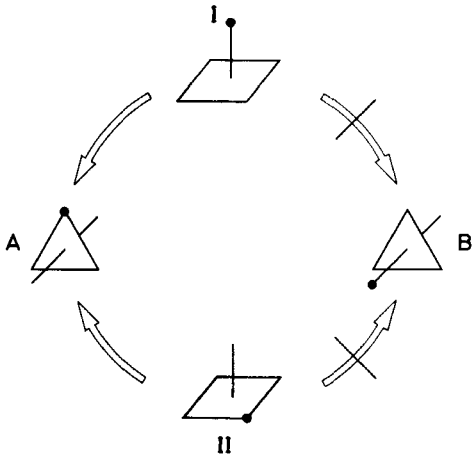

FIGURE 1 Rearrangement of the square pyramids (SP) I and II to the trigonal bipyramids (TBP) A and B; the black circle denotes the heteroligand X. The selection rules in display are only valid if the heteroaxis of the parent hexacoordinated complex is characterized by the weakest ligand field.[10]

the rearrangement paths to A and B are C_{2v} and C_s, respectively; Figure 2 can be viewed as a Woodward–Hoffmann correlation diagram. The central tetragonal structure, which is still closely related to the octahedron, has three π orbitals and two σ orbitals, whereas the trigonal structures have only two pure π orbitals and essentially three σ orbitals. Along both reaction paths therefore one π orbital acquires σ character (d_{yz} along I–A, d_{xy} along I–B).

The predominant photoactive state of Cr(III) complexes is the first excited quartet state,[14–16] corresponding to the configuration (xy xz z^2), or $\pi^2\sigma^1$. Along the I–A distortion path of Figure 2, the nature of the first excited configuration remains essentially $\pi^2\sigma^1$. The σ orbital gets even slightly stabilized and therefore the left hand side reaction is allowed. But along the I–B distortion path the nature of the d_{xy} orbital does change, and one obtains a high energy $\sigma^2\pi^1$ configuration; the reaction is forbidden.[17] Basically, the difference between the two distortions stems from the fact that the destabilized orbital belongs to a degenerate set in one case, but not in the other case. If it belongs to a degenerate set, it does not have to carry the electron, in the other case, it does. As a consequence, the square pyramid is spontaneously transformed into the ground state quartet of TBP A, characterized by the population (xy xz z^2-y^2).

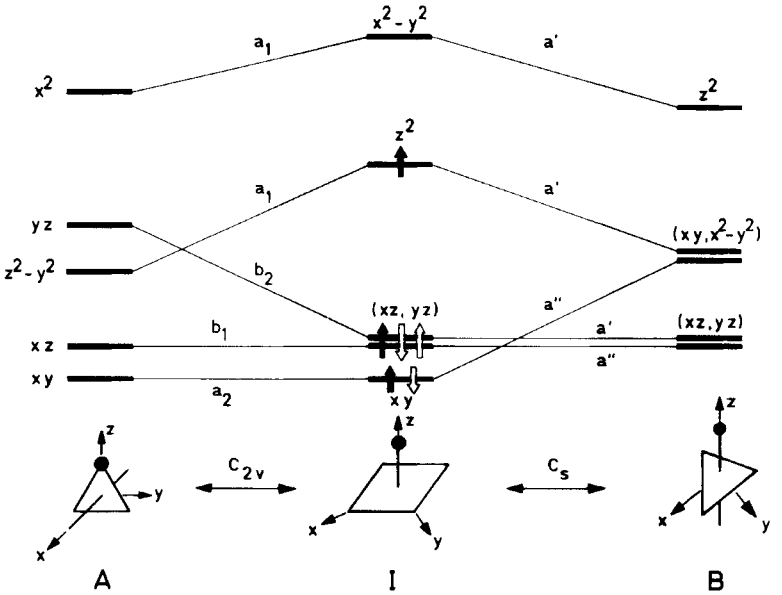

FIGURE 2 Orbital correlation diagram of SP–TBP rearrangements (the two distortions of SP I). Black arrows correspond to the orbital occupation in the first excited quartet d^3 state; the combination of black *and* white arrows corresponds to the orbital occupation in the first triplet excited d^6 state.

The situation does not change very much when one adds three more electrons, so that it is possible to discuss Co(III) and Rh(III) complexes on the basis of the same Figure 2. The first excited triplet of the tetragonal structure—corresponding to the photoactive state—has a $\pi^5\sigma^1$ configuration. Along the I–A path, this leads to $\pi^4\sigma^2$, corresponding to the lowest triplet state of the TBP A; but along the I–B path, one obtains an excited $\pi^3\sigma^3$ triplet state. Therefore, here again I → A is allowed and I → B is forbidden.[18]

A similar analysis could also be carried out for the two distortion possibilities of SP II, leading to the conclusion summarized in Figure 1. Therefore, the relevant rearrangement is I–A–II and its correlation diagram is shown in Figure 3. This diagram is of central importance in discussing all the photosubstitutions considered so far.

First consider the Cr(III) complexes.[17,19] If one starts from I, generated by an axial labilization of the parent hexacoordinated complex, the TBP is produced in its ground state, characterized by $(z^2\text{-}y^2)$ occupation. If

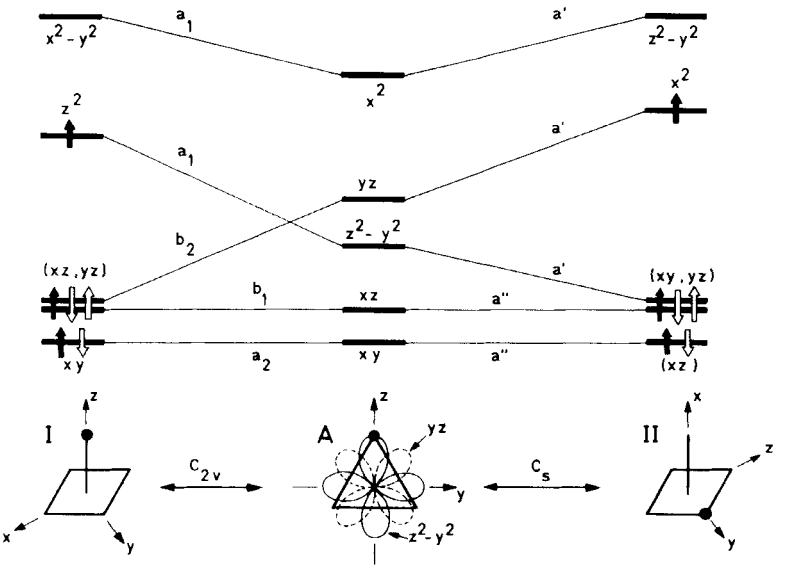

FIGURE 3 Orbital correlation diagram for the I–A–II rearrangement. The convention describing the configurations of the excited states is the same as in Figure 2. For the TBP A, only the equatorial triangle is shown; the two additional axial ligands are on the *x* axis.

one starts from II, generated by an equatorial labilization, the TBP is produced in its first excited state, characterized by yz occupation. Now, yz and $(y^2\text{-}z^2)$ are the two equatorial orbitals situated in the plane of the triangle (Figure 3); the heteroligand is situated on the $(y^2\text{-}z^2)$ orbital. The trigonal bipyramid can add a sixth ligand in essentially two ways: the incoming solvent molecule can enter in *cis* and in *trans* of the heteroligand. If $(y^2\text{-}z^2)$ is occupied yz is empty; therefore *cis* attack will be the favored process, and *trans* attack will be energetically difficult and forbidden. If on the other hand yz is occupied and $z^2\text{-}y^2$ is empty, the opposite behavior is expected: in that case, *cis* attack will be forbidden and *trans* attack will be allowed.

These conclusions on the addition of the incoming ligand can be rationalized in terms of Woodward–Hoffmann correlation diagrams, or alternatively, they might be expressed in terms of Fukui's frontier orbitals: the ligand orbitals are the HOMO's, while the metal orbitals have to be the LUMO's. Figure 4 shows a schematic representation[19] of the situation at the state level: the preference for a *cis* or a *trans*

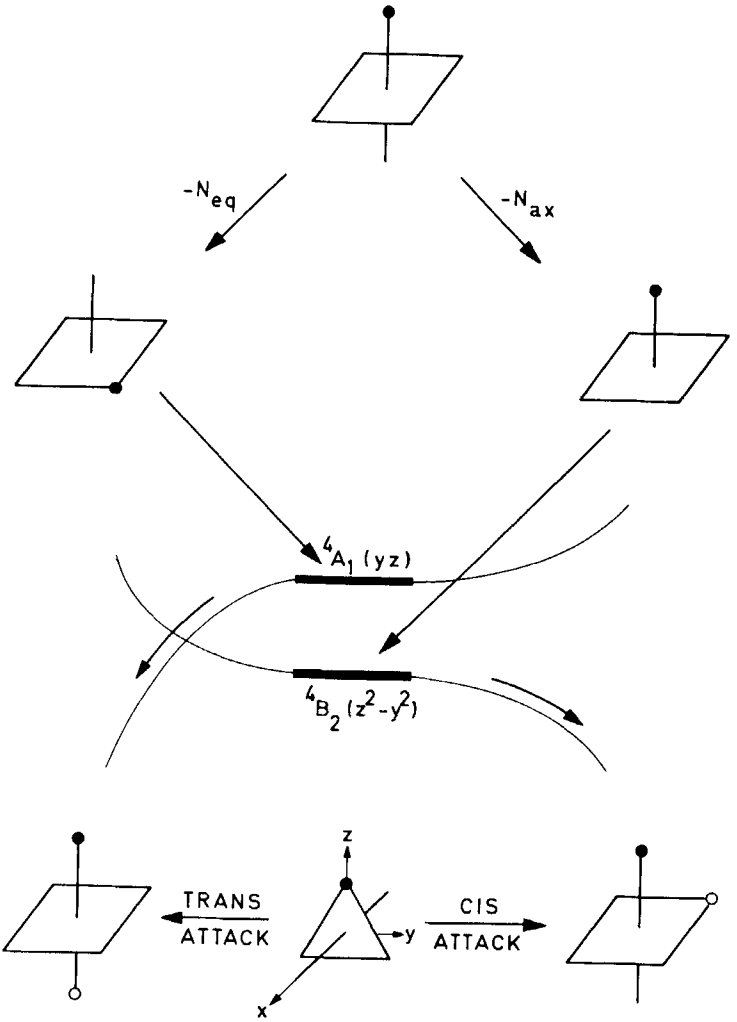

FIGURE 4 Schematic state correlation diagram for d^3 systems. A black circle represents a weak-field heteroligand; white circle represents an incoming solvent molecule.

photosubstitution product of $^4B_2$ or $^4A_1$ is readily predicted from this figure.

For axial labilization, the predictions are very well verified experimentally[17]; for equatorial labilization, the experimental data are limited, but the scheme works well for monofluoropentamine, where the addition reaction apparently takes place from the excited $^4A_1$ state.[19] The diagrams become more complicated for disubstituted complexes, but also there, the expected patterns seem to be reproduced.[10–13]

The d^6 systems, such as Co(III) or Rh(III) complexes, can also be discussed on the basis of Figure 3. However, there are a number of important differences with the Cr(III) case.[18] The most important difference is that the photoactive triplet states of I and II are now correlated to the *same* state in A, and hence to each other. Indeed from both SP's the transition to the TBP leads to doubly occupied xz and xy orbitals while yz and $(y^2\text{-}z^2)$ are singly occupied. In contrast to the Cr(III) case, where either yz or $y^2\text{-}z^2$ was vacant, the d^6 TBP triplet under consideration has *no* favorable access possibilities. Neither do the two excited SP fragments, because of the occupation of all π orbitals and the one axial σ orbital (z^2 or x^2). In fact, the only species that does offer a favorable association path is the ground state of the SP's when z^2 and x^2 are vacant. The addition then takes place in *trans* of the axial ligands. In Figure 5 the situation is sketched very schematically: the photoactive state corresponds to the lowest triplet curve. For strong field complexes [all Rh(III) complexes for instance] this triplet is the TBP ground state. Both the I–A and the II–A distortion are symmetry-allowed along the triplet surface and therefore, a selection rule by itself cannot explain the d^6 photochemistry. The detailed application of ligand field theory predicts a comparatively small barrier at the TBP. If the barrier is low enough to allow a crossing, the triplet will get concentrated in the lowest energy structure, which will act as a trap. From there intersystem crossing, will carry the complex into the SP ground state, and then to hexacoordination.

Basically, the energy difference between the two SP triplets can be traced back to the energy difference between two orbitals, namely z^2 and x^2. This energy difference can be shown to be simply proportional to the difference in σ parameters between the heteroligand X and the other four ligands L. The prediction is that the photoproduct will be *trans* when $\sigma_L > \sigma_X$, it will be *cis* when $\sigma_L < \sigma_X$. So far, this prediction has been confirmed quite satisfactorily by a large number of experi-

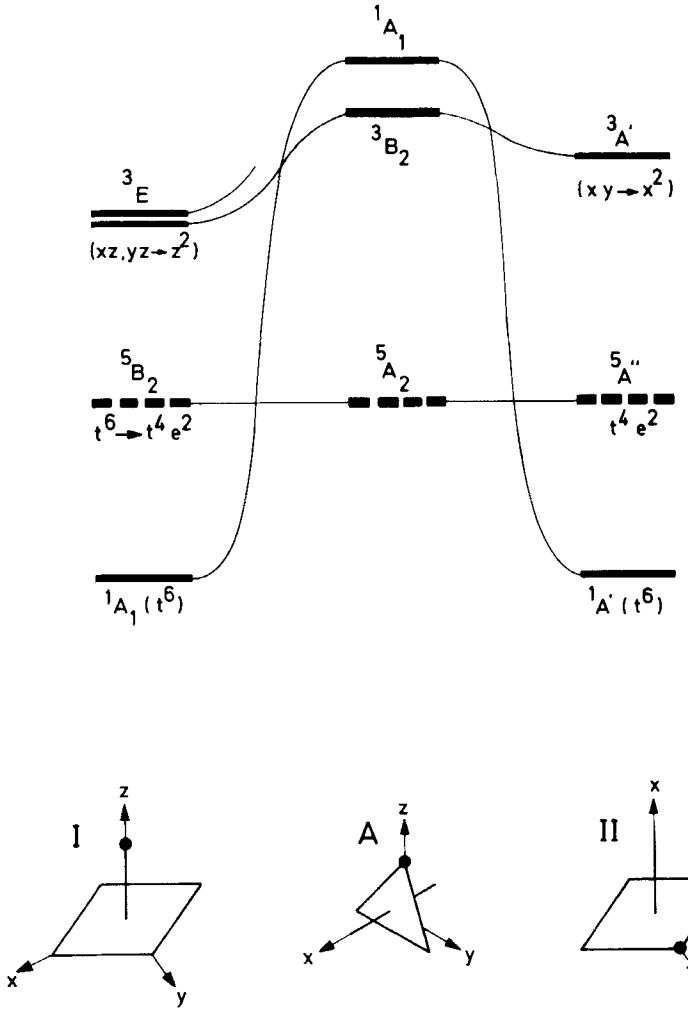

FIGURE 5 Schematic state correlation diagram for d^6 systems. If $\sigma_L > \sigma_X$ (X is a weak field heteroligand), ^3E is below $^3A'$ as shown, and *trans* addition can be expected. The quintet surface is represented by dashed lines: only for certain Co(III) and Fe(II) fragments is this quintet situated as shown between the singlet and the triplet. For stronger ligand fields, as in Rh(III) or Ir(III) compounds, the quintet is situated at higher energies well above the triplet state. For a discussion of the role of the quintet in Co(III) photochemistry, the reader is referred to Ref. 20.

mental data. Extensive comparisons between theory and experiment are available in the literature.[9,10,18]

SPIN CHANGE AND THERMAL STEREOMOBILITY

Although no detailed mechanistic descriptions are available for the thermal reactions of hexacoordinated transition metal complexes, it is possible to analyze some of these reactions in the same spirit as in the previous section. For instance, it can be shown that ligand field theory implies the necessity of a spin change along any stereomobile reaction path of any low-spin d^6 system.[21]

Stereomobility can take place in two different ways: by an intramolecular twist, or else by a dissociative mechanism, where a five-coordinated intermediate rearranges from one SP to another SP via a TBP. We will only consider the latter possibility, since it is closely related to the previous considerations. As a matter of fact, the correlation diagrams of Figures 3 and 5 are also relevant in the present context. The groundstate reaction along the singlet $^1A_1$ surface is clearly forbidden in the Woodward–Hoffmann sense, as it corresponds to a spin-conserving $\pi^6 \rightarrow \pi^4\sigma^2$ reaction. Therefore, the experimentally observed stereomobility has to be connected to a level crossing. In principle both the lowest SP triplet ($\pi^5\sigma^1$) and the lowest SP quintet state ($\pi^4\sigma^2$) are likely candidates to play a role in the thermal reactions under consideration. In the TBP, the lowest triplet $^3B_2$ is necessarily below $^1A_1$, since both states have the same configuration and the same orbital energy, but $^3B_2$ is characterized by the additional stability associated with unpaired spins (Hund's rule). The lowest TBP quintet $^5A_2$ has a less favorable orbital energy, but it is even more Hund-stabilized than the triplet.

For strong fields, such as in all Rh(III) or Ir(III) complexes, the triplet has the lower energy of the two; it remains inaccessible however, because of the large value of $Dq = 3\sigma–4\pi$ and/or the small value of the Racah B and C parameters. This fact is in agreement with the observed thermal stereoretention of the Rh(III) and Ir(III) complexes.[22,23] For weaker fields such as in the Fe(II) or certain Co(III) complexes, the quintet drops below the triplet and becomes thermally accessible. This fact may be responsible for the observed stereomobility of Co(III) β

diketonates[24–26] and the *cis–trans* isomerization of certain $Co(en)_2$ AX complexes.[17] As a general rule, the activation energy for stereomobility is found to be roughly proportional to the ligand field strength 10 Dq—in agreement with experiment.[28,29]

INTERPRETATION OF THE LIGAND FIELD PARAMETERS

The previous two sections illustrate the use of correlation diagrams in stereochemical problems. The orbital correlation diagrams could have been obtained just as well by using any approximate MOT, e.g., EHT. But the description of the state variations requires explicit consideration of the interelectronic repulsions, and here ligand field theory appears to have an advantage: the energy differences between states of different multiplicity can be parametrized just as easily as the one-electron energy differences between states of the same multiplicity. In the latter case, one needs the σ, π and Dq parameters, while in the former case, one needs the Racah repulsion parameters B, C and the spin-pairing parameter D.

Yet, in the last section of this paper, we want to focus attention on a number of recent Hartree–Fock calculations on transition metal ions and complexes. The results indicate that the physical meaning of the Racah B and C parameters does not correspond to the simple repulsion interpretation associated with them in ligand field theory. In fact, the Racah parameters (or alternatively the Slater–Condon parameters F_k) result from the application of conventional multiplet theory to atomic spectroscopy. Quite generally, multiplet theory is based on first-order perturbation theory,[30] as exemplified in Figure 6B for a d^2 system. One starts from a fixed set of five degenerate d orbitals; the specific form of these d orbitals is usually left unspecified (semiempirical multiplet theory), but the most direct way to obtain an explicit expression for the d orbital form is to solve the Hartree–Fock equations for the d^2-configuration average. On the basis of the associated repulsion integrals, the energy of the five corresponding states can then be determined unequivocally. In this view, the five states are characterized by the same one-electron energy H, and ^3F is the groundstate because it has the smallest repulsion energy C. In general, the application of conventional multiplet theory leads to very satisfactory results, at least qualitatively and even semiquantitatively. Yet, strictly speaking, the corresponding

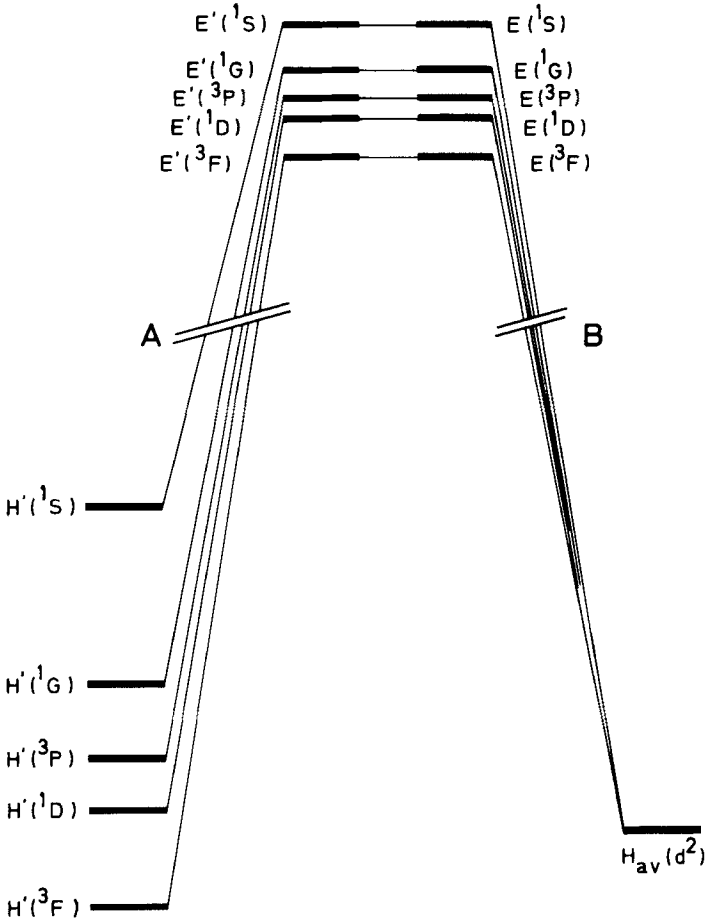

FIGURE 6 Schematic energy level diagram for a d^2 metal ion (not to scale). (A) Results of Hartree–Fock calculations for the five individual terms (L, S); E' is the total energy and H' is the one-electron energy: $E' = H' + C'$ where C' is the two-electron repulsion energy. (B) Results of one Hartree–Fock calculation on the configuration average of the d^2 configuration; by using the corresponding (frozen) orbitals and repulsion integrals, a more approximate (though very good) value for the term energies is obtained. Here too, $E = H + C$ where the unprimed symbols refer to frozen-orbital calculations; obviously $H(^3F) = H(^1D) = \cdots = H_{av}(d^2)$.

picture cannot possibly be correct, since first-order perturbation theory is obviously incompatible with the virial theorem[31]: two states, say ^3F and ^1D cannot be characterized simultaneously by the same kinetic energy T and by a different potential energy V. One has $E = T + L + C = T + V = H + C$, where L is the electron-nuclear attraction energy; the virial theorem requires $E = -T = V/2$. Yet, classical multiplet theory assumes that, for two terms of the same configuration $\Delta E = \Delta C$ and $\Delta L = \Delta T = 0$. This violation of the virial condition was not taken to be too serious, apparently because the success of multiplet theory suggested that $\Delta L + \Delta T = \Delta H \simeq 0$; this implies that one had to assume[32] an (approximate) cancellation of ΔL and ΔT.

It can be shown that this assumption is erroneous.[31,33] Indeed if a separate Hartree–Fock calculation is carried out for each individual (L,S) multiplet, the total energy E', and its one-electron part H' can be depicted as in Figure 6A. The unprimed symbols E, H, . . ., refer to the frozen orbital calculations, while the primed symbols E', H', . . ., refer to the individual multiplet calculations. The most striking feature of the figure is that the total energies—shown at the top—are very nearly equal in A and B: the error is of the order of 10^{-4}%; in absolute value, E and E' are equal to about 100 cm^{-1}. Therefore, as far as spectral energies are concerned, the frozen orbital calculations are nearly perfect. The situation is quite different for the one-electron energies $H = T + V$ (shown at the bottom of the figure). At the B side, we have only one H level, because all the orbitals are forced to remain unchanged in the five different states. At the A side, however, the orbitals are not constrained in any way and are allowed to relax to their optimal shape, depending on each individual situation. Figure 6 shows that the range of the five H' values is roughly *five times* the range of the total energies E'. Consequently, the relaxation differences corresponding to the change in shape of the orbitals are far more important than the repulsion differences. By adding the repulsion, thus in going from the bottom to the top, the level sequence of the A side remains unaltered, but the energy gaps are considerably compressed. The five d^2 terms therefore behave in a completely nonconventional way: the repulsion energy *decreases* from ^3F to ^1D to ^3P to ^1G to ^1S—exactly the opposite result as obtained from first-order perturbation theory. The Racah parameters apparently incorporate more one-electron energy differences than two-electron (repulsion) energy differences.

This line of thinking can be extended[33] by calculating for all d^n systems

the average spin pairing energy necessary to change the spin quantum number from S to $S - 1$. If $4 \leq n \leq 6$, three different multiplicities are possible, and from first-order perturbation theory, it can be shown that for a given set of (frozen) orbitals,

$$\frac{E(S-1) - E(S)}{E(S-2) - E(S-1)} = \frac{C(S-1) - C(S)}{C(S-2) - C(S-1)} = \frac{S}{S-1}, \quad (1)$$

where for instance $E(S)$ represents the weighted mean total energy and $C(S)$ the weighted mean repulsion energy of the multiplets characterized by S. On the basis of the Hellmann–Feynman theorem, it can be shown that to a very good approximation one obtains the *same* equation from separate Hartree–Fock calculations:

$$\frac{E'(S-1) - E'(S)}{E'(S-2) - E'(S-1)} \simeq \frac{C'(S-1) - C'(S)}{C'(S-2) - C'(S-1)} \simeq \frac{S}{S-1}, \quad (2)$$

where for instance $E'(S)$ is obtained directly from the Hartree–Fock equation for the weighted mean energy of the d^n multiplets characterized by S. It is a remarkable fact that Eqs. (1) and (2) lead to the same ratio, although for instance $C(S-1) - C(S)$ and $C'(S-1) - C'(S)$ are of opposite sign! This result illustrates in a very striking way how conventional multiplet theory can lead to correct predictions on a rather fictitious basis.

It is well to stress here that the nonclassical variation of the repulsion energy from one multiplet to another is not limited to transition metals. The same behavior is observed in first-row atoms, where the phenomenon was reported many years ago[34]: of the three carbon $2p^2$ terms, ^3P has the highest interelectronic repulsion. For the dipositive and higher ions of the first row, however, the classical behavior reappears[31] and the repulsion of O^{++} $2p^2$ increases from ^3P to ^1D to ^1S. For transition metal atoms and ions on the contrary, the nonclassical results are obtained for all chemically important oxidation states.[33]

It would be interesting to extend these ideas to transition metal complexes. Two preliminary remarks can be made at this point: (i) In order to explain the reduced value of the Racah parameters in a molecular complex, Jørgensen[35] suggested a connection between the increased

open shell volume (accompanying covalency) and decreased interelectronic repulsion. While this idea seemed quite natural in the framework of conventional multiplet theory, it becomes very questionable from the present point of view.[33,36] (ii) Preliminary Hartree–Fock calculations on the $Cr(CN)_6^{3-}$–t_{2g}^3 states reproduce the $^4A_2$, ^2E, $^2T_1$ and $^2T_2$ states in the correct order, but here again the interelectronic repulsion *decreases* from $^4A_2$ to $^2T_2$, in direct opposition to the ligand field predictions.[37]

CONCLUSIONS

Ligand field theory, especially in its AOM version, is a viable alternative to qualitative molecular orbital theories. It clearly has predictive value in the study of stereochemical aspects of transition metal complexes. Especially in treating interelectronic interactions in the open d shell, the method offers a simple and convenient way of describing the evolution of the relevant states along the appropriate reaction coordinates. Yet, to the extent that ligand field theory gives the right answers, it does so—at least in part—for the wrong reasons. Much remains to be done in elucidating the exact nature of the ligand field parameters, and in understanding why such an utterly simple and partly unsound model turns out to be so useful.

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37. L. G. Vanquickenborne, to be published.