electron density between methoxy and phenoxy oxygens and the lengthening of two Fe–O bridging bond distances from 2.05 to 2.18 Å are almost magnetically invisible since the methoxophenoxo- and the diphenoxo-bridged complexes show not significantly different J values.

Whether or not the effects of the two longer Fe–O bond distances and the reduced electron density in the Salen^{2-} derivative are counterbalanced by other factors such as the effect of one larger bridging angle at oxygen or the planarity of the bridging unit remains unknown.

In summation, when it is considered collectively, the evidence of the properties of the three complexes does not indicate any unequivocal magnetostructural relationship. This result, although rather disappointing, is not totally surprising. Although the effects on the ordering of spin states of geometrical distortions and of substituent changes for a variety of Cu(II) dimers could be accounted for[7,8] by analyzing, in terms of pairwise interactions of dimeric MO's, only the direct superexchange mechanism (coupling with ionic states), a very recent ab initio direct calculation[24] of the singlet-triplet separation in cupric acetate hydrate dimer has shown that at least other three essential contributions (whose dependence on structural changes in the system has still to be analyzed) must be considered in order to quantitatively understand the observed magnetic properties. The problem is easily predicted to be greatly complicated by the presence of five electrons per atom.

Acknowledgment. The authors are indebted to Dr. D. Fiorani for his assistance in the securing of magnetic measurements at liquid-helium temperatures and to Mr. V. Jorio for his drawing.

Registry No. $Fe_2L(OCH_3)Cl_2$, 81028-21-9.

Supplementary Material Available: Listings of the hydrogen atom coordinates and the observed and calculated structure factor amplitudes for $Fe_2L(OCH_3)Cl_2$ (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Leuven, 3030 Heverlee, Belgium

On the Meaning of Spin-Pairing Energy in Transition-Metal Ions

L. G. VANQUICKENBORNE* and L. HASPESLAGH

Received September 23, 1981

Conventional multiplet theory predicts a number of well-verified regularities for the spin-pairing energy in transition-metal ions. In the present work, these predictions are analyzed at the Hartree–Fock level. It is shown that many regularities persist in the SCF wavefunctions and energies but that the interpretation of the results is quite different. The implications for other parts of multiplet theory and ligand field theory are briefly discussed.

Introduction

In ligand field theory, the formation of high-spin vs. low-spin transition-metal complexes is considered to result from the interplay of two opposing tendencies. On the one hand, the ligand field induces one-electron energy differences between the metal d orbitals; the larger these differences, the more the lower lying orbitals will tend to be fully occupied. On the other hand, the complete occupation of these orbitals and the corresponding spin pairing is taken to be hindered by the larger repulsion, characterizing two electrons with opposite spins. The properties of the complex can be described by considering the balance of some typical one-electron ligand field parameter ($10Dq$ in octahedral complexes) and the so-called spin-pairing energy. Within the framework of the conventional multiplet theory,[1] this spin-pairing energy is an interelectronic repulsion energy and can be expressed in terms of the Racah B and C parameters or alternatively in terms of the Slater–Condon integrals F^k.

The most general treatment of the spin-pairing energy has been given by Jørgensen[2] and Slater;[3] on the basis of first-order perturbation theory, they show that, for any nd^q configuration

$$E(S) = E(nd^q) + [\overline{S(S+1)} - S(S+1)]D$$

where $E(nd^q)$ is the weighted mean energy of the configuration, $E(S)$ is the weighted mean energy of the multiplets characterized by S spin quantum number, $\overline{S(S+1)}$ corresponds to the average value of the total spin angular momentum, and D is a typical metal parameter. Therefore

$$\Delta E = E(S-1) - E(S) = 2SD \qquad (1)$$

It is clear that ΔE provides the neatest way to describe the average effect of changing the spin of just one electron. For d^q systems, where more than two multiplicities are possible (q = 4–6) this means that

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

The relevant quantity is then $\Delta E/2S = D$, the spin-pairing parameter; it is a measure for the energy required to change just two electrons from unpaired (↑↑) to paired (↑↓). For all nd^q systems, D is given by one single parametric expression,[2,3] eq 2. It can also be shown that D is proportional to the

$$D = {}^{7}/_{12}(5B + 2C) = {}^{5}/_{84}[F^2(nd;nd) + F^4(nd;nd)] \qquad (2)$$

average exchange integral K_{av} of the d^q system: $D = {}^{7}/_{6}K_{av}$.

Since the Racah repulsion parameters B and C are inherently positive, D and ΔE are also positive; therefore eq 1 goes some length toward the rationalization of Hund's first rule.

It is well-known that this first-order perturbation approach leads to very satisfactory results: nearly all the predictions of the classical multiplet theory are qualitatively and semiquantitatively verified by extensive spectral data for nearly all the elements of the periodic system.

Yet, for certain first-row atoms and ions, a detailed comparison of first-order perturbation theory and SCF calculations

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Table I. Total Energy and Energy Components of the Five States, Corresponding to the Ti^{2+}, $3d^2$ Ion[a]

(A) SCF Calculation for Each Individual State

	E'	L'	T'	H'	C'
^3F	−847.731	−1998.045	847.731	−1150.314	302.583
^1D	−847.680	−1997.767	847.680	−1150.087	302.406
^3P	−847.670	−1997.721	847.670	−1150.051	302.381
^1G	−847.652	−1997.614	847.652	−1149.962	302.309
^1S	−847.542	−1996.950	847.541	−1149.409	301.867

(B) Calculations Based on the Frozen Orbitals of the SCF Average of Configuration

	E	L	T	H	C
^3F	−847.731				302.417
^1D	−847.680				302.467
^3P	−847.670	−1997.840	847.693	−1150.147	302.478
^1G	−847.652				302.496
^1S	−847.536				302.611

[a] All energies are in hartrees. E is the total energy, L is the electron–nuclear attraction energy, T is the kinetic energy, $H = L + T$ is the one-electron energy, C is the repulsion energy. The unprimed symbols refer to the frozen orbital approximation, while the primed symbols to the individual Hartee-Fock calculations.

has revealed rather surprising results. For instance, both C and O^{2+} are characterized by a ground configuration $2p^2$, leading to ^3P, ^1D, and ^1S. First-order perturbation theory predicts that the interelectronic repulsion increases from ^3P to ^1D to ^1S. From SCF calculations, this result is verified for O^{2+} but not for C, where the reverse order is obtained![4-6] This surprising effect is not an artifact of the SCF calculations: it is completely confirmed by more exact methods.[5-8]

In the light of these results it seems worthwhile to reexamine the picture offered by conventional multiplet theory. Does it remain true—at the SCF level—that the spin-pairing energy in transition-metal ions is basically an interelectronic repulsion effect, as implied by eq 1 and 2? So that this matter could be investigated, a number of numerical Hartree–Fock calculations[9,10] were carried out for di- and tripositive ions of the transition metals.

A Simple Example: Ti^{2+} ($3d^2$). Before considering the spin-pairing problem in general, it is instructive to look at a simple example calculation. For the Ti^{2+} ion, a $3d^2$ system, separate SCF calculations were carried out for the five different states ^3F, ^1D, ^3P, ^1G, and ^1S individually; the results are shown in Table IA and Figure 1A. For comparison, we also carried out a Hartree–Fock calculation of the configuration average d^2; using the frozen orbitals of this average, it is possible to obtain an alternative (and more approximate) value for the energies of the individual multiplets (L, S). These results are also shown in Table IB and Figure 1B. A calculation of the latter type is in principle the best possible treatment within the framework of the conventional multiplet theory.

The energy components are denoted as follows: L is the electron–nuclear attraction energy, C is the interelectronic repulsion energy, T is the kinetic energy, V is the potential energy, and H is the one-electron energy: $E = T + L + C = T + V = H + C$. The primed symbols E', T', etc. refer to direct Hartree–Fock results while the unprimed symbols are reserved for frozen-orbital calculations.

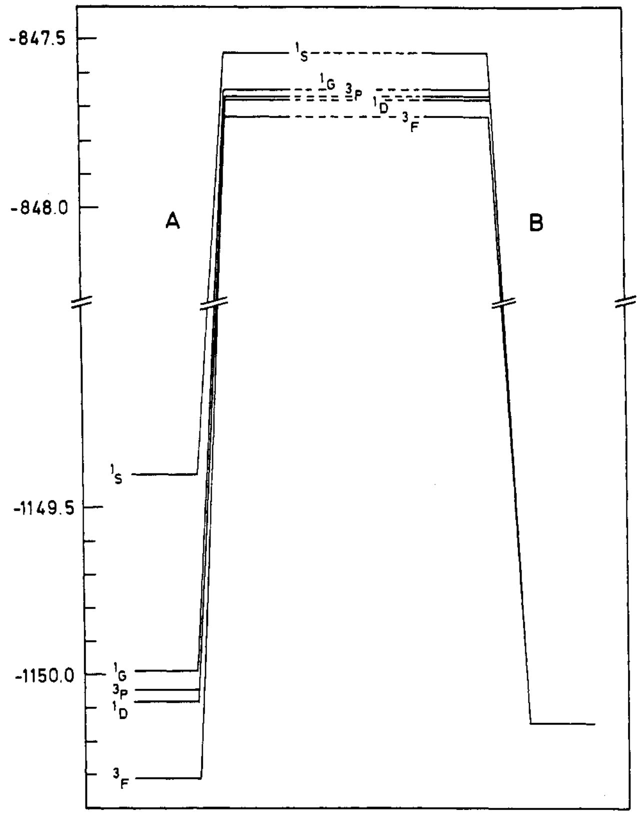

Figure 1. Total energy E (central part of the figure) and one-electron energy $H = L + T$ (left- and right-hand side) of the five states, resulting from the $3d^2$ configurations of Ti^{2+}: (A) SCF calculations for each individual state; (B) calculations based on the frozen orbitals of the SCF average of configuration (in hartree units). L is the electron–nuclear attraction energy, and T is the kinetic energy.

Table IA and IB predict essentially the same total energy $E \simeq E'$. The relative values of E agree qualitatively with the available spectral data; the correct order is predicted in spite of the exchange correlation difference between singlets and triplets.[11] Quantitatively, the energy differences are in error by ~20%.

The most striking point of Table IA is that the repulsion energy C' *decreases* from the lowest to the highest excited states; the ^3F ground state is characterized by a larger interelectronic repulsion than any other state of the $3d^2$ configuration. This result is in obvious contradiction to the commonly accepted ideas on metal ion multiplets, which are exemplified in Table IB. The frozen-orbital calculation implies one common value of L and T for all multiplets, and therefore the energy difference between any two terms simply equals their repulsion difference. The ^3F ground state is then of course calculated with the smallest value of C.

One basic deficiency of the frozen-orbital calculations is that they cannot possibly provide a correct partition of the energy into its components: being based on first-order perturbation theory, they interpret ΔE as a result of ΔV only, leaving ΔT as 0—a procedure which clearly violates the virial theorem.

The exact Hartree–Fock solutions of Table IA on the contrary do satisfy the virial theorem $E' = -T'$. Therefore the ^3F ground state is also characterized by the largest kinetic energy. This implies that the electron–nuclear attraction L' and not the interelectronic repulsion C' is the decisive factor in determining the relative energy of the multiplets $L'(^3F) < L'(^1D) < L'(^3P) < L'(^1G) < L'(^1S)$.

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Table II. Hartree–Fock Spin-Pairing Energy $D' = \Delta E'/2S$ and Its Components for the Dipositive Transition-Metal Ions V^{2+} through Ni^{2+} (cm^{-1})[a]

	D	D'	$\Delta L'/2S$	$\Delta T'/2S$	$\Delta C'/2S$	$\Delta C'_c/2S$	$\Delta C'_{cd}/2S$	$\Delta C'_{dd}/2S$
(d^2) Ti^{2+}	6459	6432	35 853	−6432	−22 989	12283	−40 337	5065
(d^3) V^{2+}	7017	7044	35 353	−7045	−21 264	10800	−36 635	4571
(d^4) Cr^{2+} A	7554	7631	35 342	−7631	−20 080	9705	−33 935	4150
B	7554	7515	35 698	−7514	−20 669	9702	−34 264	3893
(d^5) Mn^{2+} A	8076	8199	35 627	−8199	−19 229	8853	−31 857	3775
B	8076	8079	35 959	−8078	−19 802	8842	−32 149	3505
(d^6) Fe^{2+} A	8580	8630	36 413	−8629	−19 154	8149	−30 457	3154
B	8580	8556	36 601	−8557	−19 488	8138	−30 613	2987
(d^7) Co^{2+}	9079	9089	37 198	−9090	−19 019	7560	−29 219	2640
(d^8) Ni^{2+}	9571	9564	38 006	−9564	−18 878	7058	−28 135	2199

[a] All Δ's refer to the energy for the smaller S value minus the energy for the large S value. $\Delta C'_{dd}$ refers to the repulsion associated with the $3d^q$ occupation only, $\Delta C'_c$ to the intracore repulsion, and $\Delta C'_{cd}$ to the intershell repulsion between core and d electrons. For comparison, the first column shows $D = \Delta E/2S$, calculated from the frozen orbitals of the configuration average.

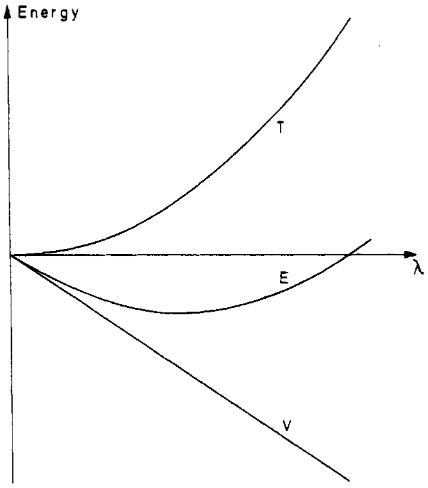

Figure 2. Evolution of the total energy E and the kinetic (T) and potential (V) components as a function of a scaling factor λ. The virial theorem is satisfied for the minimum in E, where $\lambda = -V/2T$. Increasing λ corresponds to a contraction of the wave function, decreasing λ to an expansion.

In Figure 1, these results are displayed in a slightly different way: the central part shows the total energies, and at the two sides, we show the one-electron energies H or H'. While H is represented by one single level at the right-hand side of the diagram, the H' range at the left-hand side is roughly five times larger than the E or E' ranges! The frozen-orbital calculations apparently neglect the larger effects and incorporate the E differences effectively into the smaller effects (the C variations).

Starting from the frozen-orbital calculation of any given multiplet, the exact Hartree–Fock solution can be obtained by allowing the orbitals to relax to their optimal shape. Although the total relaxation energy is virtually zero, the energy components do change significantly upon relaxation. This can be understood most easily by considering the relaxation process essentially as an expansion or a contraction.[7] In fact, the introduction of a scaling factor λ can account for more than 95% of the relaxation effects on V or T while at the same time reconciling the results with the virial theorem. Figure 2 shows the evolution of E, T, and V as a function of the scaling factor λ. As a consequence of the variation principle, a small change in λ will not affect E in the neighborhood of its minimum, while the T and V components are very sensitive—but compensating—functions of λ. Near the energy minimum, $dE/d\lambda \simeq 0$ and $dV/d\lambda \simeq -dT/d\lambda \simeq V$.

Calculation of Spin-Pairing Energies. In order to come as close as possible to the perturbation approach[2,3] of Jørgensen and Slater, it is indicated to solve the Hartree–Fock equations for the weighted mean of the multiplets characterized by a given spin quantum number and to obtain the energy $E'(S)$. For instance in the case of $3d^2$, it should be sufficient to carry out two separate SCF calculations, one for $E'(1)$, the weighted average of ^3F and ^3P, and another one for $E'(0)$, the weighted average of ^1D, ^1G, and ^1S. In general $\Delta E' = E'(S-1) - E'(S)$, $\Delta L' = L'(S-1) - L'(S)$, etc. Figure 3 and Table II show the variation of $\Delta E'/2S$, $\Delta L'/2S$, $\Delta T'/2S$, and $\Delta C'/2S$ as a function of Z for the dipositive ions of the first transition series. If the number of d electrons is denoted by q, and the degree of ionization by p, Figures 3 and 4 are characterized by $p = 2$ and $q = Z - 20$. Figure 4 offers an alternative representation of the total energy differences $\Delta E'$. It is possible to maintain eq 1 at the SCF level so that $\Delta E'/2S$ can be considered as the Hartree–Fock value of the spin-pairing energy D'.

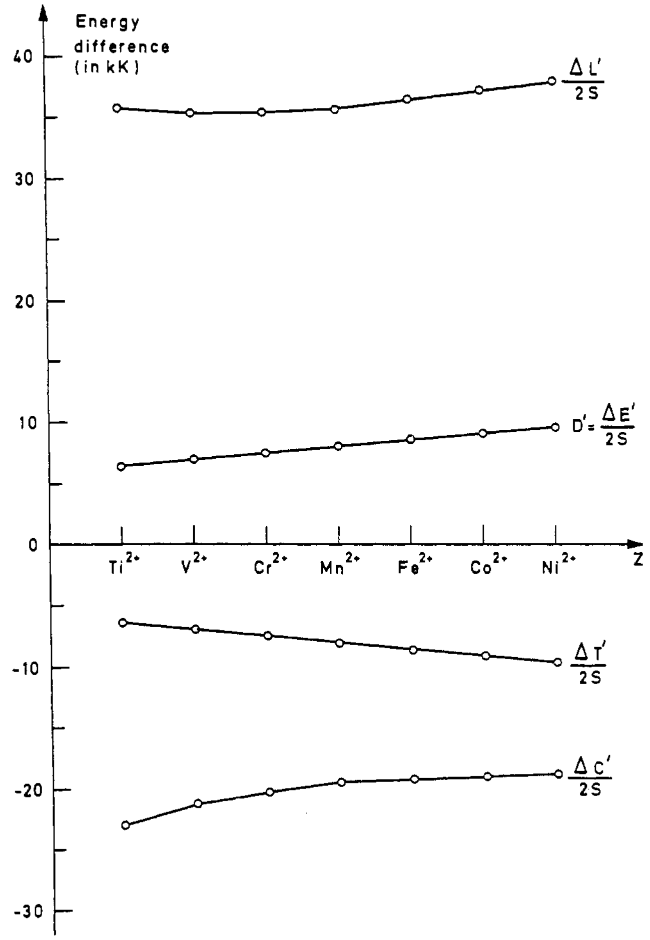

Figure 3. Variation of the Hartree–Fock spin-pairing energy $D' = [E'(S-1) - E'(S)]/2S$ and its components for the dipositive ions of the first transition series ($p = 2$) as a function of Z, or $q = Z - p - 18$.

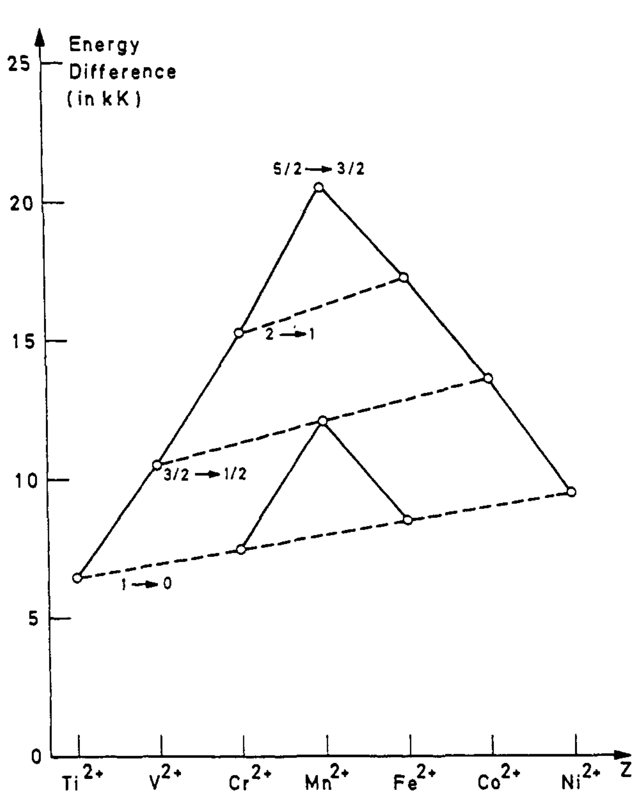

Figure 4. Hartree–Fock spin-flip energy differences $\Delta E' = E'(S - 1) - E'(S)$ for the dipositive $3d^q$ systems.

First of all, it should be stressed that the so calculated D' values agree fairly well with the semiempirical data based on eq 2. While the range in Figure 3 is from 6430 cm^{-1} for Ti^{2+} to 9560 cm^{-1} for Ni^{2+}, the corresponding experimental curve[12] runs smoothly parallel from 5420 cm^{-1} for Ti^{2+} to 8660 cm^{-1} for Ni^{2+}.

This implies in the first place that the calculated D' values are all positive, which was not a priori obvious since D' is now composed of $\Delta L'$, $\Delta C'$, and $\Delta T'$ contributions. It means that—also at the Hartree–Fock level—spin pairing is an energy-requiring process. This conclusion was to be anticipated from the results obtained for the Ti^{2+} example. Indeed, using frozen orbitals of the configuration average $3d^q$ (introduced in the previous section), it is possible to calculate (albeit somewhat less accurately) the average energy of the terms with spin S. The so-obtained energy will be denoted $E(S)$ in order to distinguish it from $E'(S)$, the result of the direct Hartree–Fock solution. In analogy to the results for Ti^{2+} (Table I), one finds $E(S) \simeq E'(S)$, and $E(S - 1) \simeq E'(S - 1)$: the relaxation from the (global) configuration average to the (partial) average of the states with constant spin is negligible. For $E(S - 1)$ and $E(S)$, eq 1 and 2 apply and therefore $\Delta E' \simeq \Delta E > 0$.

For the same reason, the two D' values of d^4, d^5, and d^6 corresponding to the transitions $(S \rightarrow S - 1)$ and $(S - 1 \rightarrow S - 2)$ are very nearly identical (Table II, Figure 3). The proportionatlity of ΔE and S, implied by eq 1, can be transferred to the Hartree–Fock values $\Delta E'$ without a significant loss of accuracy.

Analysis of the Spin-Pairing Energy Components. While the frozen-orbital calculations are characterized by $\Delta T = \Delta L = 0$ and $\Delta C = \Delta E > 0$, Figure 3 shows the mirror symmetry between the $\Delta E'$ and $\Delta T'$ curves, as imposed by the virial thereom. The most remarkable result, however, is that $\Delta C'$ is negative throughout. All the dipositive transition-metal ions apparently behave in a nonconventional way: the interelectronic repulsion *increases* with S. In this sense, the transition metals are different from the first-row elements considered in ref 4–8, where the unexpected repulsion differences were observed for the neutral atoms but not for the dipositive or higher positive ions.

Table III. Orbital Radii r_i (au) of the Core and Valence Orbitals of the Ti^{2+} Ion

	$S = 1$	$S = 0$	$3d^2$ av
1s	0.070 116	0.070 116	0.070 116
2s	0.325 062	0.325 058	0.325 061
2p	0.289 562	0.289 555	0.289 560
3s	1.014 406	1.013 583	1.014 132
3p	1.089 389	1.088 093	1.088 958
3d	1.392 461	1.422 261	1.402 201

Therefore, in the transition-metal ions under consideration, spin pairing does require a positive energy; however, this energy is not a repulsion energy, but it is predominantly a nuclear-attraction energy. Indeed, since $\Delta E' > 0$, $\Delta C' < 0$, and $\Delta T' < 0$, $\Delta L'$ has to be positive and dominant.

For d^4, d^5, and d^6 ions, let us denote the two relevant transitions by $A(S \rightarrow S - 1)$ and $B(S - 1 \rightarrow S - 2)$. From the virial theorem $\Delta E'_A = -\Delta T'_A$, $\Delta E'_B = -\Delta T'_B$. Since $\Delta E'_A/2S \simeq \Delta E'_B/2(S - 1)$, one also has $\Delta T'_A/2S \simeq \Delta T'_B/2(S - 1)$ and the two $\Delta T'$ points are very nearly superposed in Figure 3 (within a few hundred reciprocal centimeters). So would $\Delta V'_A/2S$ and $\Delta V'_B/2(S - 1)$, but the virial theorem by itself does not require the superposition of the two points for the repulsion and the attraction components separately. The fact that this nevertheless is found to be the case (Figure 3) can most easily be understood from the Hellmann–Feynman theorem. If the nuclear charge is allowed to be variable, one has for any given metal ion, and for the three cases $(S, S - 1, S - 2)$

$$dE'/dZ = L'/Z$$

and, hence, for both A and B

$$d\Delta E'/dZ = \Delta L'/Z$$

Since $\Delta E'_A/2S \simeq \Delta E'_B/2(S - 1)$ for all Z, the derivatives will also be equal and therefore

$$\Delta L'_A/2S \simeq \Delta L'_B/2(S - 1) \tag{3a}$$

$$\Delta C'_A/2S \simeq \Delta C'_B/2(S - 1) \tag{3b}$$

A remarkable aspect of eq 3b is its formal equivalence to the frozen-orbital expression $\Delta C_A/2S = \Delta C_B/2(S - 1)$. Yet ΔC and $\Delta C'$ have opposite sign, and numerically, they differ by a factor 2–3.

Interelectronic Repulsion Components. Figure 5 and Table II show a further breakdown of $\Delta C'$ into its components: $\Delta C'_{dd}$ is the repulsion associated with the $3d^q$ occupation only, $\Delta C'_c$ is the intracore repulsion, and $\Delta C'_{cd}$ is the intershell repulsion between core and d electrons. The following points may be noticed.

(i) $\Delta C'_{dd} > 0$. The d–d repulsion plays the key role in the frozen-orbital calculations, where $\Delta E = \Delta C = \Delta C_{dd} > 0$ and $\Delta C_c = \Delta C_{cd} = 0$. So at least ΔC_{dd} and $\Delta C'_{dd}$ have the same sign. The commonly accepted idea that the d–d repulsion increases with decreasing S remains valid; it is connected to the differential exchange correlation, associated with spin change. It should be stressed, however, that $\Delta C'_{dd}$ is numerically the smallest component of $\Delta C'$.

(ii) $\Delta C'_c > 0$. The intracore repulsion, which is unchanged in the frozen-orbital approximation, increases with decreasing S. Spin pairing thus induces a core contraction; this conclusion is confirmed by a calculation of the average radius of the core orbitals (Table III).

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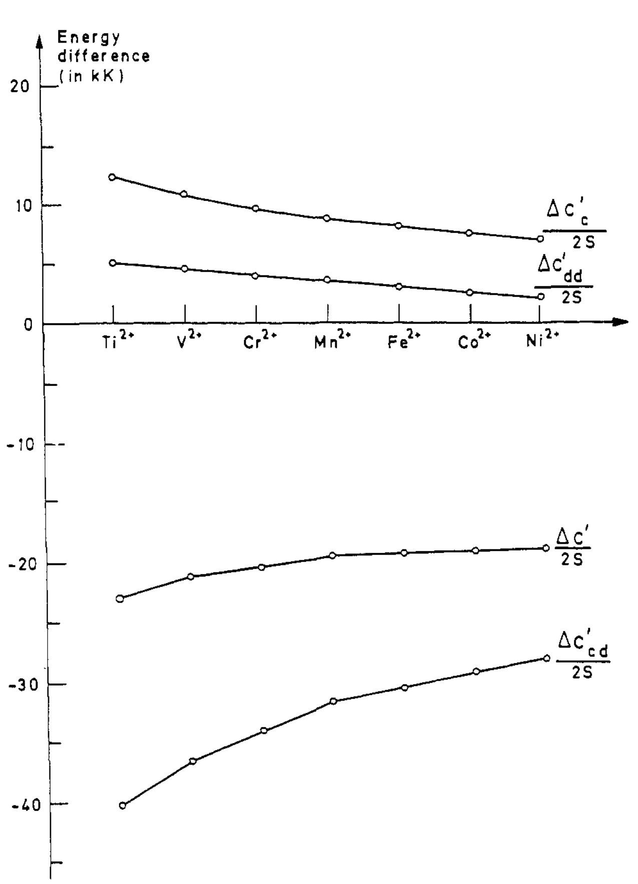

Figure 5. Decomposition of the interelectronic repulsion energy differences $\Delta C'$ as a function of Z for the dipositive ions of the first transition series. $\Delta C'_{dd}$ refers to the repulsion associated with the $3d^q$ occupation only, $\Delta C'_c$ to the intracore repulsion, and $\Delta C'_{cd}$ to the intershell repulsion between core and d electrons. The $\Delta C'/2S$ curve is identical with the one in Figure 3.

(iii) $\Delta C'_{cd} < 0$. The intershell repulsion (also unchanged in the frozen-orbital approximation) strongly decreases with decreasing S. In fact, $\Delta C'_{cd}$ is by far the leading term in ΔC: it is roughly three times larger than the other two terms together. Part of this effect is related to the core contraction, but the main reason for the C'_{cd} decrease is a considerable expansion of the 3d orbitals as a consequence of spin pairing.

Again, this conclusion is confirmed by a calculation of the orbital radii. Table III shows the results for the Ti^{2+} ion.

The observations i–iii are quite similar to what has been found in the analysis of first-row atoms;[6] they provide us with some insight in the nature of the relaxation process. Suppose we start from the average of the $3d^q$ configuration, characterized by the orbitals φ_i and total energy $E(3d^q)$. If S_{min} is the lowest possible spin value of this configuration, $E(S_{min})$ calculated on the basis of the frozen φ_i orbitals will satisfy $E(S_{min}) > E(3d^q)$ because $C_{dd}(S_{min}) > C_{dd}(3d^q)$. These inequalities can be expressed in terms of the Racah parameters or the Slater–Condon $F^k(3d;3d)$ integrals.

The relaxation of the φ_i orbitals to $\varphi_i'(S_{min})$ amounts essentially to an expansion of the 3d orbitals accompanied by a (much smaller) core contraction. One of the manifestations of the 3d expansion is the decrease of the $F^k(3d;3d)$ repulsion integrals. Therefore $C_{dd}(S_{min}) > C'_{dd}(S_{min})$; the repulsion increase from $C_{dd}(3d^q)$ to $C_{dd}(S_{min})$, inherent in the frozen-orbital calculation, is attenutated by the relaxation process. In all cases considered in Figure 5, however, this attenutation preserves the relative order of the d–d repulsions, i.e., $C_{dd}(S_{min}) > C'_{dd}(S_{min}) > C_{dd}(3d^q)$. The expansion of the 3d orbitals also withdraws some electron density from the inner-shell region, leading to a (rather limited) core contraction. The interplay of both effects results in such a significant decrease of the interelectronic repulsion that the relative order of the total repulsion *does* get reversed: while $C(S_{min}) > C(3d^q)$ before relaxation, $C'(S_{min}) < C(3d^q)$ after relaxation. Although the Pauli correlation is minimal for S_{min}, relaxation effects will operate in such way that the average interelectronic separation will be *larger* for S_{min}.

Precisely the opposite behavior is observed for S_{max}, the largest possible spin value. In that case $E(S_{max}) < E(3d^q)$, and the relaxation process from the configuration average to the high-spin states can be adequately described by a 3d contraction, accompanied by a limited core expansion. The 3d contraction again attenutates the originally imposed decrease in d–d repulsion, without inverting the relative order; for the total repulsion on the contrary, the order is inverted, and $C'(S_{max}) > C(3d^q) > C'(S_{min})$.

For intermediate spin states, contraction or expansion is observed, depending on the relative value of $E(S)$ and $E(3d^q)$.

The detailed description of the relaxation process shows why the spin-pairing energies in Figure 3 are always larger than the repulsion energy differences $\Delta C'_{dd}/2S$ in Figure 5. Indeed

$$2SD' = \Delta E' \simeq \Delta E = \Delta C = \Delta C_{dd} > \Delta C'_{dd}$$

The latter inequality represents the attenuation of the d–d repulsion increase in the transition $S \rightarrow S - 1$.

For d^4, d^5, and d^6 systems, the different components of $\Delta C'/2S$ remain superposed (or very nearly so) for the two transitions involved (denoted A and B in the previous section): $(\Delta C'_{dd})_A/2S \simeq (\Delta C'_{dd})_B/2(S - 1)$, etc. This result can be rationalized to some extent by considering the relaxation as a simple scaling process (expansion from S to $S - 1$ to $S - 2$). Then it is not difficult to show[13] that the scaling parameters λ_A and λ_B are given by $\lambda_A \simeq 1 - (D/T)S$ and $\lambda_B \simeq 1 - (D/T)(S - 1)$; hence

$$\begin{aligned}(\Delta C'_{dd})_A &\simeq 2SD(1 - (C_{dd}/2T))\\ (\Delta C'_{dd})_B &\simeq 2(S - 1)D(1 - (C_{dd}/2T))\end{aligned} \tag{4}$$

In these equations the first term is simply the d–d repulsion difference, calculated from the frozen orbitals of the $3d^q$ average, that is, $(\Delta C_{dd})_A$ or $(\Delta C_{dd})_B$; the second term is the relaxation energy. Therefore, in the scaling approximation, the relaxation energy is simply proportional to the first-order energy differences $\Delta E_A \simeq \Delta E'_A$ and $\Delta E_B \simeq \Delta E'_B$ and

$$\frac{(\Delta C'_{dd})_A}{(\Delta C'_{dd})_B} \simeq \frac{(\Delta C_{dd})_A}{(\Delta C_{dd})_B} = \frac{\Delta E_A}{\Delta E_B} = \frac{S}{S - 1} \tag{5}$$

The same conclusion will remain essentially valid for a nonuniform scaling (contraction of the core, expansion of the 3d shell) or for the exact SCF relaxation. Indeed, Table II is in rather satisfactory agreement with eq 5. The repulsion energies $C'_{dd}(S)$, $C'_{dd}(S - 1)$, and $C'_{dd}(S - 2)$ can be expressed as linear combinations of the $F^k(3d;3d)$ integrals, which we denote $F^k{}_S$, $F^k{}_{S-1}$ and $F^k{}_{S-2}$, respectively. From the data in Table IV, eq 6 can be verified for all k, in agreement with eq 5.

$$\frac{(\Delta F^k)_A}{(\Delta F^k)_B} = \frac{F^k{}_{S-1} - F^k{}_S}{F^k{}_{S-2} - F^k{}_{S-1}} \simeq \frac{S}{S - 1} \tag{6}$$

Role of Nuclear Charge Z. If $p = 2$ (Figure 3), $D' = \Delta E'/2S$ is an increasing function of Z; this can be connected to the fact that $D' \simeq D$ (Table II). Within the frozen-orbital

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(13) In general, the scaling factor is given by $\lambda = -V/2T$ (see also Figure 2). In this derivation, one also uses the fact that ΔC_{dd}, based on the orbitals of the configuration average, is not modified significantly when one uses another set of orbitals (corresponding to $E(S)$, $E(S - 1)$, or $E(S - 2)$) *for both terms of the difference*. Indeed, not only $\Delta E \simeq \Delta E'$ but also $\Delta E \simeq \Delta E_S \simeq \Delta E_{S-1} \simeq \Delta E_{S-2}$, where the latter three symbols denote the energy difference based on the frozen orbitals, corresponding to $E(S)$, $E(S - 1)$, and $E(S - 2)$, respectively. Therefore $D \simeq D' \simeq D_S \simeq D_{S-1} \simeq D_{S-2}$.

Table IV. F^k(3d;3d) Integrals for the Hartree–Fock Calculations Corresponding to $S_{\max}$, $S_{\max} - 1$, $S_{\max} - 2$, and the Configuration Average for 3d^4, 3d^5, and 3d^6 Systems (in hartrees)

		F^0	F^2	F^4
Cr^{2+}	$S = 2$	0.781 43	0.363 55	0.226 57
	$S = 1$	0.770 25	0.356 45	0.221 77
	$S = 0$	0.764 62	0.352 89	0.219 36
	3d^4	0.770 25	0.356 45	0.221 77
Mn^{2+}	$S = {}^5/_2$	0.838 76	0.390 19	0.243 16
	$S = {}^3/_2$	0.828 03	0.383 33	0.238 51
	$S = {}^1/_2$	0.821 55	0.379 20	0.235 72
	3d^5	0.824 43	0.381 04	0.236 96
Fe^{2+}	$S = 2$	0.884 42	0.409 51	0.254 82
	$S = 1$	0.877 47	0.405 05	0.251 80
	$S = 0$	0.873 98	0.402 82	0.250 29
	3d^6	0.877 47	0.405 05	0.251 80

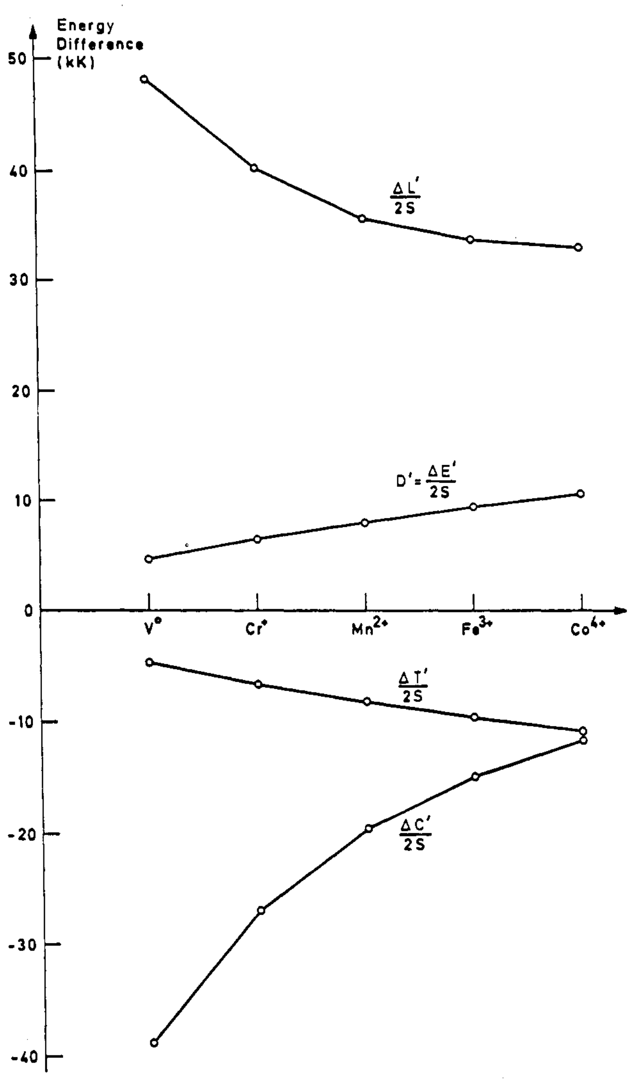

Figure 6. Evolution of the Hartree–Fock spin-pairing energy $D' = [E'(S-1) - E'(S)]/2S$ and its components for the 3d^5 ions ($q = 5$) as a function of Z, or $p = Z - q - 18$.

approximation, D is given by one single parameteric expression for all Z (eq 2). Since the F^k(3d;3d) integrals for the configuration average are increasing functions of Z (see also Table III), the conventional approach[1] predicts that

$$\Delta C_{dd}/2S = \Delta C/2S = \Delta E/2S$$

will increase with Z.

From the preceding sections, it now appears that the D' evolution should be interpreted in a very different way. Indeed, the Hartree–Fock calculations reveal (Figure 5, Table II) that the d–d repulsions $\Delta C'_{dd}$ *decrease* with Z. This can be understood by looking at the detailed expressions[1-3] for C_{dd} as a function of the F^k integrals:

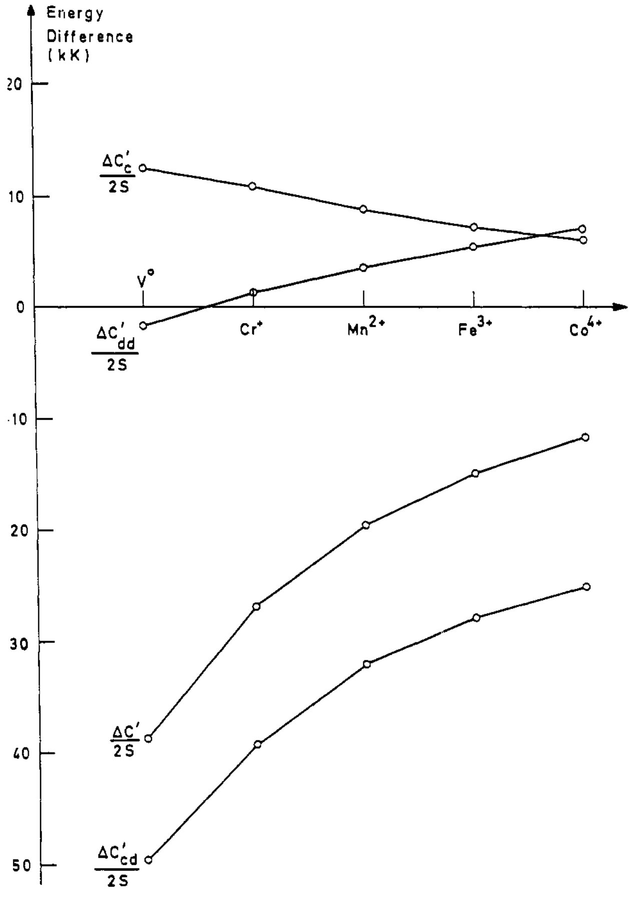

Figure 7. Decomposition of the interelectronic repulsion energy differences $\Delta C'$ as a function of Z or p for $q = 5$. The $\Delta C'/2S$ curve is identical with the one in Figure 5.

$$C_{dd} = (q(q-1)/2)F^0 + [{}^3\!/_4 q - {}^{21}\!/_{60} q(q-1)]D - S(S+1)D$$

If the specific set of F^k integrals, obtained for a given value of S, are again denoted $F^k{}_S$ and if further $D_S = {}^5/_{84}(F^2{}_S + F^4{}_S)$, $\Delta F^k = F^k{}_{S-1} - F^k{}_S$, and $\Delta D = D_{S-1} - D_S$, one obtains eq 7.

$$\Delta C'_{dd} = C'_{dd}(S-1) - C'_{dd}(S) = (q(q-1)/2)\Delta F^0 + [{}^3\!/_4 q - {}^{21}\!/_{60} q(q-1)]\Delta D - S(S-1)\Delta D + 2SD_S \quad (7)$$

The last term in eq 7 corresponds to the difference in d–d repulsion, calculated from the frozen orbitals of the S multiplets: one has[13] $2SD_S \sim 2SD = \Delta C_{dd}$. The other terms of eq 7 describe the relaxation within the d shell; ΔF^0 and ΔD are negative and correspond to the attenuation of the d–d repulsion (discussed in the previous section). In the relaxation term $|\Delta F^0| >> |\Delta D|$, and the dominant contribution is proportional to $q(q-1)$. This explains the decrease of the d–d repulsion from Ti^{2+} to Ni^{2+}, in spite of the increase of all the F^k(3d;3d) integrals. Therefore, the curves of $\Delta C_{dd}/2S \simeq \Delta E'/2S$ (Figure 3) and $\Delta C'_{dd}/2S$ (Figure 5) as a function of Z are divergent.

If one keeps the number of d electrons constant, while varying the degree of ionization, p, one obtains a somewhat different situation, which is exemplified in Figure 6 and 7 for the $q = 5$ case. The basic pattern of Figures 3 and 5 is confirmed, although there are a few points that require additional comment.

In the first place, since both figures refer to d^5 systems, one has to consider two transitions: A(${}^5/_2 \rightarrow {}^3/_2$) and B(${}^3/_2 \rightarrow {}^1/_2$). In fact, *all* the points on both figures are very nearly the superpositions of two points: the difference between the two relevant D' values is always of the order of 100 cm^{-1}.

In Figure 5, the evolution of the three energy components $\Delta L'$, $\Delta C'$, and $\Delta T'$ as a function of Z is completely determined by the $\Delta E'(Z)$ curve. Indeed, since the number of electrons is constant, the combination of the virial theorem and the Hellmann–Feynman theorem imposes unambiguous relations between the three energy components.

It has been shown[6,7] that the conventional behavior ($\Delta C > 0$) tends to reappear at increasing degree of ionization (also evident from Figure 5). Yet, the present calculations show that even for Co^{4+}, $\Delta C'$ remains negative and rather large in absolute value (of the order of several electronvolts).

The slope of D' as a function of Z is roughly 3 times larger in Figure 6 than in Figure 3. An increase of the slope is to be expected from conventional arguments[1] although, again, the interpretation of this phenomenon is definitely more complex.

The most striking difference between Figures 5 and 7 is the sign inversion in the slope of $\Delta C'_{\text{dd}}$ as a function of Z. In the present case ($q = 5$), the curves $\Delta C'_{\text{dd}}/2S$ and $\Delta E'/2S \simeq \Delta C_{\text{dd}}/2S$ do not diverge but rather they are roughly parallel. The reason is immediately obvious from eq 7, where the dominant relaxation term $q(q-1)\Delta F^0/2$ now only varies on account of ΔF^0, which is not a very sensitive function of Z. In fact for neutral V, one calculates a negative value of $\Delta C'_{\text{dd}}$: the absolute value of the relaxation energy exceeds the classical repulsion increase. As a consequence, one obtains the rather exceptional case where the repulsion decreases *even within the 3d shell.*

Finally, a third way to investigate the role of Z is to modify the principal quantum number n. A number of example calculations for both di- and tripositive ions show that the same basic conclusions remain valid in this case.

Concluding Remarks

1. For a number of typical transition-metal ions, the Hartree–Fock spin-pairing energy has been shown to consist essentially of nuclear-attraction contributions and much less of electron-repulsion contributions (see Figures 1 and 3). As a matter of fact, spin pairing, the transition from $\uparrow\uparrow$ to $\uparrow\downarrow$, is characterized by a *decrease* of the electronic repulsion. From the analogy with the results obtained for the first-row atoms and ions,[6] it may be conjectured that our conclusions are valid for all chemically relevant transition-metal ions—not only at the Hartree–Fock level but probably also for the exact solutions.

2. The connection with first-order perturbation theory can be made by calculating the different term energies and their spin averages $E(S)$ on the basis of the frozen orbitals of the configuration average.

Apparently, the success of conventional multiplet theory rests on the fact that the relaxation energy $E'(S) - E(S)$ is negligibly small. Because of this fact, the classical theory does have a predictive value: the sign, the magnitude, and the evolution of the spin-pairing energy as a function of p, q, or Z are all correctly predicted. Moreover, the dependence of the $F^k(3d;3d)$ integrals of these same variables is also qualitatively as expected from simple shieldings considerations. Yet, at the Hartree–Fock level, both facts are not just cause and effect, as they are in conventional multiplet theory. Rather they are interrelated in a much more intricate manner, leading to a very different interpretation of the spin-pairing energy. In fact, for a constant degree of ionization, the classical ΔC_{dd} increases with Z, while the Hartree–Fock $\Delta C'_{\text{dd}}$ decreases with Z (Figures 3 and 5).

3. For $q = 4$–6, the energies $\Delta E'_{\text{A}}$ and $\Delta E'_{\text{B}}$, as well as their different components, are very nearly in the ratio $S/(S-1)$. The reason for this fact was not obvious from a direct Hartree–Fock treatment. It is apparently profitable to start from the less accurate theory where eq 1 and 2 are readily deduced; at the SCF level, the near validity of eq 1 has been shown to entail a whole series of near equalities

$$\frac{\Delta E'_{\text{A}}}{\Delta E'_{\text{B}}} = \frac{\Delta T'_{\text{A}}}{\Delta T'_{\text{B}}} \simeq \frac{\Delta L'_{\text{A}}}{\Delta L'_{\text{B}}} \simeq \frac{\Delta C'_{\text{A}}}{\Delta C'_{\text{B}}} \simeq \frac{(\Delta C'_{\text{dd}})_{\text{A}}}{(\Delta C'_{\text{dd}})_{\text{B}}} \simeq \frac{\Delta F^k{}_{\text{A}}}{\Delta F^k{}_{\text{B}}} \simeq \frac{(\Delta C'_c)_{\text{A}}}{(\Delta C'_c)_{\text{B}}} \simeq \frac{(\Delta C'_{\text{cd}})_{\text{A}}}{(\Delta C'_{\text{cd}})_{\text{B}}} \simeq \frac{\Delta E_{\text{A}}}{\Delta E_{\text{B}}} = \frac{\Delta C_{\text{A}}}{\Delta C_{\text{B}}} = \frac{(\Delta C_{\text{dd}})_{\text{A}}}{(\Delta C_{\text{dd}})_{\text{B}}} = \frac{S}{S-1}$$

Particularly remarkable in this sequence is $\Delta C'_{\text{A}}/\Delta C'_{\text{B}} \simeq \Delta C_{\text{A}}/\Delta C_{\text{B}}$ where the primed (Hartree–Fock) and unprimed (conventional) quantities are of different sign!

4. In principle, the considerations on the $\Delta E'_{\text{A}}/\Delta E'_{\text{B}}$ ratios might also be applied to other parts of multiplet theory where certain definite energy ratios are predicted. For instance, in the $2p^2$ configuration, the ratio $[E(^1\text{S}) - E(^1\text{D})]/[E(^1\text{D}) - E(^3\text{P})]$ is predicted to equal 3/2.

From the previous considerations, one should expect nearly the same ratio for the Hartree–Fock energy differences and their components. In principle this is true, but the numerical errors amount to ~5% for $\Delta E'$ and up to ~20% for certain components. The reason why the agreement is much less satisfactory than for the spin-pairing results is connected to the fact that $E'(S)$, $E'(S-1)$, etc. are themselves (partial) averages; the errors on the individual terms will tend to cancel.

5. The correct interpretation of $\Delta E'$ as a combination of one- and two-electron energy differences leads to a picture which is quite different from the conceptual frame offered by the classical theory. Within this frame, which is also the basis for ligand field theory, it seemed very natural to connect the nephelauxetic effect in metal complexes to the decreased repulsion accompanying the d-orbital covalency.[14] This interpretation has already been questioned on the basis of direct ab initio calculations on octahedral complexes.[15] From the present point of view, a connection between reduced term separations and d–d repulsions or covalency cannot really be expected in the first place.

Acknowledgment. The authors are grateful to Professor W. C. Nieuwpoort and his group (Groningen, The Netherlands) for help with the numerical Hartree–Fock program. They are also indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid).

Registry No. Ti^{2+}, 15969-58-1; V^{2+}, 15121-26-3; Cr^{2+}, 22541-79-3; Mn^{2+}, 16397-91-4; Fe^{2+}, 15438-31-0; Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5.

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