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Application of the 'Singular Value Decomposition' Method for the Quantitative Interpretation of the NMR Spectra of Paramagnetic Compounds

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A possible new application for the 'singular value decomposition' (SVD) method is described. With the help of SVD, the isotropic NMR shifts of paramagnetic metallorganic compounds of the type $Cp_3Ln \cdot B$ (where Cp = η^5-cyclopentadienyl, B = neutral base and Ln = lanthanoid) were quantitatively interpreted in terms of dipolar and contact shifts. A brief review of alternative approaches to separate dipolar and contact shifts is given, and the new method based on SVD is shown to be superior on statistical grounds. © **1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

Mathematical–statistical methods are having an ever increasing impact on chemistry. The method of 'singular value decomposition' (SVD), which allows the computation of generalized eigenvalues of matrices,[1] is used (especially as the mathematical basis for 'factor analysis') for many different purposes.[2] For example, in NMR spectroscopy SVD is a valuable alternative to the Fourier transformation in the interpretation of time domain signals.[3]

The so-called 'shift reagents' represent a wide and important research field in NMR spectroscopy.[4,5] The quantitative interpretation of the arising shifts ('isotropic shifts') has often been tried with various approaches,[6–14] but none of them has been generally recognized as being a standard method. This paper describes the application of SVD and the superiority of this approach over all hitherto presented methods.

Organometallic lanthanoid compounds of the type[15] $Cp_3Ln \cdot B$ (Cp = η^5-cyclopentadienyl, B = neutral base and Ln = lanthanoid) (Fig. 1) were chosen as model samples. They have the great advantage of being sufficiently soluble without any modification, even in non-polar organic solvents. This feature eliminates the otherwise non-negligible problem of ligand exchange. Furthermore, it can be assumed that the molecular structures in solution agree with those determined by x-ray analyses.

THEORETICAL BACKGROUND[16]

The so-called 'isotropic shift', defined as the difference in the NMR shifts of a diamagnetic reference compound and the examined paramagnetic compound, is made up by several parts. In practice, minor contributions such as nuclear Zeeman or quadrupole terms are neglected, leaving the dipolar (or pseudo-contact) and the (Fermi) contact shift:

$$\Delta_{iso} = \delta_{dia} - \delta_{para} = \Delta_{dip} + \Delta_{con} \quad (1)$$

Dipolar shift

The dipolar shift is usually described by the point dipole–point dipole interaction model, giving

$$\Delta_{dip} = GD + G'D' \quad (2)$$

where G and G' are the so-called geometry factors [where $G = (3\cos^2\upsilon - 1)/r^3$, $G' = \sin^2\upsilon \cos 2\varphi/r^3$; r, υ and φ are polar coordinates of the measured nucleus with respect to the paramagnetic center] and D and D' describe the magnetic anisotropy of the compound [$D = (\chi_{xx} + \chi_{yy} - 2\chi_{zz})/6N_A$, $D' = (\chi_{yy} - \chi_{xx})/2N_A$; N_A = Avogadro's constant].

To simplify the following discussion, only axially symmetric compounds ($D' = 0$) will be considered (but this is not a necessary condition, see below). Furthermore, experimental data[10] indicate that the validity of the point dipole model for ^{13}C nuclei is doubtful (possible spin transfer via p orbitals), so this paper implicitly only deals with ^{1}H nuclei.

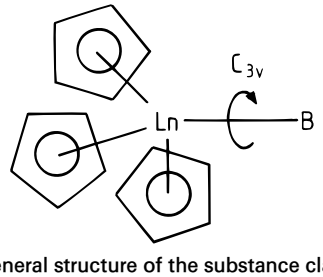

Figure 1. General structure of the substance class $Cp_3Ln \cdot B$.

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Contact shift

The contact shift is caused by through-bond spin transfer and is given by

$$\Delta_{con} = AX \tag{3}$$

where A is the (super-)hyperfine coupling parameter and $X = \langle S \rangle / (N_A \beta \beta_N g_N)$ the electron spin density experienced by the measured nucleus (β = Bohr magneton, β_N = nuclear magneton, g_N = nuclear g factor, $\langle S \rangle$ = expectation value of the spin density operator $\mu\hat{S}$).

The temperature dependence of D and X usually follows a (modified) Curie–Weiss law, $\chi = a/T + b$, where a and b are caused by the first- and second-order Zeeman effect, respectively. (Because of the large crystal field strength of the compounds[15] investigated here, the conditions for applying Bleaneys basic equation[17] are not met.) In practice, the Δ_{iso} *vs.* $1/T$ curves are only approximately straight lines.

THE FUNDAMENTAL SYSTEM OF EQUATIONS

In the practice of NMR spectroscopy of paramagnetic compounds, usually a series of measurements are made on (say) m nuclei at n different temperatures. For a given compound, G and A depend only upon the coordinates of the measured nucleus relative to the paramagnetic center, and D and X upon the temperature. By adding appropriate indices i ($1 \leqslant i \leqslant m$) for every nucleus and j ($1 \leqslant j \leqslant n$) for every temperature, from Eqns (1)–(3) the following fundamental equation can be derived (renaming Δ_{iso} to V_{ij}):

$$V_{ij} = G_i D_j + A_i X_j \text{ (for all } i, j) \tag{4}$$

Several different variables of Eqn system (4) may be individually found by experiment, e.g.:

(i) $m \times n$ isotropic shifts V_{ij};
(ii) m geometry factors G_i, if the molecular structure is known;
(iii) possibly m hyperfine coupling parameters from an EPR or ENDOR measurement;
(iv) n magnetic data values for D_j and X_j (if the wavefunctions of the crystal field states are completely known);
(v) alternatively, only n values for X_j from a susceptibility measurement [via $\langle S \rangle \approx (g_L - 1)/g_L \chi$, where g_L = Landé g factor of the ground manifold].

Consequently, the aims of the NMR analysis may differ and extend from checking the validity of Eqn system (4) to computing the G_i (if the molecule geometry is of primary interest) or computing the D_j and X_j (to obtain information about the crystal field wavefunction).

The Eqn system (4) also may be written in a block matrix form.[15] By defining the $(m + 2) \times (n + 2)$ matrix $\mathbf{M}$

$$\boldsymbol{M} = \begin{vmatrix} 1 & 0 & \boldsymbol{G} \\ 0 & 1 & \boldsymbol{A} \\ \boldsymbol{D} & \boldsymbol{X} & \boldsymbol{V} \end{vmatrix} \tag{5}$$

(where $\mathbf{G}$ is the $m \times 1$ matrix $|G_1\ G_2 \ldots|$ etc.), the whole Eqn system (4) (and all equations which may be derived from it) can be condensed into the mathematical equivalent statement $\text{Rank}(\mathbf{M}) = 2$.

EARLIER APPROACHES

Many attempts have been made to find methods for separating dipolar and contact shifts. Most of them have been described by DeBoer *et al.*,[14] so only a summary is given here.

The solution of the bilinear, usually highly overdetermined, Eqn system (4) can be simplified, if for certain i, j one of the summands equals zero. This is the case when either one of the factors F_k ($F_k = G_i, A_i, D_j, X_j$) is zero, or when $F_{k_1} = F_{k_2}$, $k_1 \neq k_2$. In the latter case a new 'dummy' F_{k_3}, which is zero, may be defined by subtracting the corresponding equations.

Almost all of the earlier approaches fit neatly into this scheme (which allows exactly eight possibilities).

The isotropic case: Gd(III)

If an isotropic ligand field is present, the dipolar shift vanishes, so that $D_j = 0$ for all j. This case rarely ever happens. A central ion with an $L = 0$ ground manifold is another possibility for having $D_j = 0$. Hence if such an ion exists, the separation of the dipolar and contact shifts for another member of its corresponding homologous series is straightforward. While this is a very common approach for the d-elements,[4] where the pair Co(II)–Ni(II) is used, for the lanthanoids only Gd(III) fulfils the above condition. Unfortunately, this system has an extremely long relaxation time and therefore gives rise to very broad signals. This explains why this approach has been tried only a few times.[6,7]

Combination of several lanthanoids

The Pinkerton and Spiliadis (P–S) approach is based on their *ad hoc* postulate[8] that for a homologous series of compounds with different lanthanoids the hyperfine coupling parameters are independent of the nature of the paramagnetic center, which means $A_{i_1} = A_{i_2}$. Actually the indices i_1 and i_2 do not refer to the measured nucleus, but to the paramagnetic center, so a scaling of the shifts relative to the individual magnetic properties of the paramagnetic centers has to be done. (The scheme described above still applies, however.) Computation in line with this approach gives a direct cancelling of the contact shifts of a lanthanoid pair.

A more critical discussion will be made later, where results contradicting this *ad hoc* hypothesis are described.

Extrapolation of Curie–Weiss lines

A nucleus whose distance from the paramagnetic center is far enough (say 3–4 σ bonds) usually has a negligibly small contact shift ($A_i = 0$). The approach suggested by Oroschin,[9] and examined more closely by Breitbach[10] (O/B), is based on this heuristic observation. The shifts

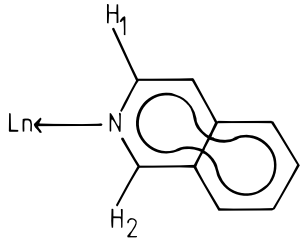

Figure 2. The coordinated isoquinoline ligand.

of all nuclei fulfilling the above condition can be extrapolated to a common (fictive) temperature T_0, where also the dipolar shift vanishes. This, in turn, allows the separation of contact and dipolar shifts of other nuclei in the same molecule, by also extrapolating their Curie–Weiss lines to T_0.

Another approach based on the temperature dependence of Δ_{iso}

Following Bleaney,[17] dipolar and contact shifts have different temperature dependences (T^{-2} and T^{-1}, respectively). This supposition also allows the separation of the shifts by extrapolation. This has sometimes been done,[11,12] but this premise is rather doubtful.[18]

Unexplored ideas

If two geometrically equivalent but chemically non-equivalent atoms ($G_{i_1} = G_{i_2}$, see Fig. 2) can be found in the same molecule (or maybe even in two different ones, as long as D and X are similar), the difference of their shifts would equal the difference of their contact shifts. In the system $Ln(dpm)_3 \cdot$ isoquinoline(dpm = 2,2,6,6-tetramethylheptane-3,5-dionato), several ppm differences in the shifts of the α protons were observed.[19] This magnitude should be high enough to give significant results, and encouraged our own study on $Cp_3Ln \cdot$ isoquinoline, which is currently under way.

The method is not generally applicable, but it could be used for verifying the usefulness of the other approaches, because it allows direct access to the contact shifts.

Fictive cases

The remaining cases are: $G_i = 0$ (only possible for a fictive geometry with the 'magic angle'), $D_{j_1} = D_{j_2}$ and $X_{j_1} = X_{j_2}$ (impossible if the temperature dependence is monotonic, e.g. a Curie–Weiss line) and $X_j = 0$ (no paramagnetism!).

Other approaches

Van Zijl *et al.* described[13] a method which directly relates the quadrupole splitting of deuterium atoms to the dipolar shift. This is an interesting approach, but it contains some special assumptions which render it inapplicable for the general case.

Summing up, for an arbitrary compound usually only the P–S and O/B approaches appear to be feasible (unless further simplifications are made).

CRITICIZING THE APPROACHES: MATHEMATICAL CONSIDERATIONS

Richardson *et al.*[20] emphasized the importance of checking the validity of the statistical methods used in order to avoid drawing false conclusions from innocent-looking NMR data. In this sense, the following subtle mathematical facts should be considered.

The Eqn system (4) can also be interpreted geometrically: the isotropic shifts V_{ij} lie (in hyperspace) on a plane which is generated by the two unit vectors dipolar shift and contact shift. Finding the components of V_{ij} with respect to this unit vectors is now hampered by a 'conspiracy' of the following circumstances:

(i) atoms 'near' the paramagnetic center have large values of G and A, whereas those 'far' from the center display only small values; in the extreme case $G_i/A_i \approx$ constant;
(ii) neglecting the second-order Zeeman effect gives $D_j/X_j \approx$ constant;
(iii) usually the dipolar shift is much larger than the contact shift (inserting common values of G, A, D and X, one obtains ratios of the order of 10:1).

This means in geometrical terms that the unit vectors are nearly parallel and of very different lengths (in matrix formulation: **V** has 'nearly' rank 1). It is intuitively clear that under these circumstances (and the statistical errors have not even been included in these considerations yet) it is very difficult to extract the smaller component of V_{ij} (the contact shift). These facts cause the O/B method (and related schemes) to have grave disadvantages, as follows:

First, the O/B method can only proceed if at least two geometry factors G_1 and G_2 are known beforehand and the temperature dependence of the shifts shows (usually Curie–Weiss) straight lines. However, as the whole O/B scheme in summary is mathematically equivalent[15] to stating that for any three atoms

$$\begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ G_1 & G_2 & G_3 \end{vmatrix} = 0 \qquad (6)$$

(a ascent of the Curie–Weiss straight lines, b axis segment, solve after G_3 while knowing G_1 and G_2), the always occurring slight curvatures of the lines produce a fairly large error in the values of b_i and therefore (as above, also this matrix has 'nearly' rank 1) an even larger error in the computation of G_3. Furthermore, the system of all equations of type (6) is not self-consistent, so the results for G_3 depend on which atoms were chosen for supplying G_1 and G_2. [It is possible to modify[15] the O/B approach slightly to avoid at least the missing self-consistency; also note that the condition $A_i = 0$ is completely superfluous for Eqn (6).]

ABANDONING LINEARITY: SVD AS A COMPLETELY NEW METHOD

As the basic idea of O/B is useful, our own new method was developed[15] to overcome its mathematical weaknesses, which is also applicable for a non-linear Δ_{iso} *vs.*

$1/T$ curve. It will now be presented (neglecting the finer mathematical details).

The central error of the hitherto described approaches is that they 'look the wrong way through the telescope:' they effectively are equivalent to picking out some 3×3 determinant of **M**, setting it to zero and solving for the unknowns. This leads to an error propagation, which can become, as explained earlier, arbitrarily large. As a warning example, the results of Breitbach[10] regarding $(MeCp)_3Nd \cdot \gamma Pic$ (γPic = 4-methylpyridine, MeCp = methylcyclopentadienyl) shall be considered (Table 3, see below), where the error propagation, due to a nearly vanishing minor, took an estimated[15] value of *ca.* 200:1, which explains the unreasonable results.

However, the 'telescope' effect can also be used in the desirable direction! Exactly this is made possible by SVD. This method takes the matrix **M** [from the definition in Eqn (5) of **M** it is clear how to include known data for G, D, A and X], and performs a least-squares fit
of the V_{ij} to the optimum possible plane. This produces a self-consistent matrix **M′**, which can now be evaluated just like the last steps of the O/B approach without facing any of its problems. Effectively, the highly overdetermined (and unfulfillable) problem $\mathrm{Rank}(\mathbf{M}) = 2$ turns into the highly underdetermined (and fulfillable) problem $\mathrm{Rank}(\mathbf{M}') = 2$, $\|\mathbf{M} - \mathbf{M}'\| = \min$ (where the double bars denote the Euclidian matrix norm).

Short mathematical description of SVD

1. Put up **M** (size $m \times n$).
2. Diagonalize $\mathbf{M}\mathbf{M}^+$ and $\mathbf{M}^+\mathbf{M}$ ($\mathbf{M}^+$ denotes the transpose of **M**) to find **L**, **R**: $\mathbf{L}^+\mathbf{M}\mathbf{M}^+\mathbf{L} = \mathbf{I}_n$ and $\mathbf{R}^+\mathbf{M}^+\mathbf{M}\mathbf{R} = \mathbf{I}_m$ (I_k means a unity matrix of size $k \times k$).
3. Compute $\mathbf{W} = \mathbf{L}^+\mathbf{M}\mathbf{R}$. **W** contains at most $\min(m, n)$ values $\neq 0$ which are the singular values.
   In application to the O/B method, find **M′** with $\mathrm{Rank}(\mathbf{M}') = 2$, $\|\mathbf{M} - \mathbf{M}'\| = \min$. as follows:
4. Set every value of **W** to zero, except the two largest ones.
5. Call this **W′** and compute $\mathbf{M}' = \mathbf{L}\mathbf{W}'\mathbf{R}^+$. **M′** is a self-consistent version of **M**.
6. Evaluate **M′** (instead of **M**) by the O/B method.

If the compound is non-axial and the term $G' \times D'$ is to be included, in step 4 'two' must be replaced by 'three.' Then, however, the application of the O/B method meets another problem: the occurrence of Curie–Weiss straight lines automatically implies $\mathrm{Rank}(\mathbf{M}) \leqslant 2$ (for any temperatures, only two measurements are linearly independent), so the third singular value is zero anyway, and there is no way to distinguish between axial and non-axial contributions! This may be the true cause (instead of spatial averaging) of the observation that so many non-axial compounds virtually behave as if they were axial.

The superior effectiveness of the SVD method was demonstrated by a number of case studies made by the author.[15] Once again it must be emphasized that SVD only redistributes the errors on all variables, and does not annihilate them. It is clear that with values of, say, $\Delta_{iso} = 110$ ppm, $\Delta_{dip} = 100$ ppm and $\Delta_{con} = 10$ ppm, an error of 10% in the second value (caused by, say, an inaccurate G_i value) invariably is connected with an error of 100% in the third one. No approach, however sophisticated it may be, can overcome this simple statistical fact.

Simple illustration of the error redistribution by SVD

Let

$$\boldsymbol{M}_1 = \begin{vmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{vmatrix}$$

$$\boldsymbol{M}_2 = \begin{vmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 8 \end{vmatrix}$$

$$\boldsymbol{M}_3 = \begin{vmatrix} 0.9 & 2.1 & 3.3 \\ 4.1 & 4.9 & 5.7 \\ 7.3 & 7.7 & 8.1 \end{vmatrix}$$

Suppose that $\mathbf{M}_2$ is a matrix of experimental values. $\mathbf{M}_1$ then symbolizes the results of applying the O/B method; the sum $\sum$ of the error squares is 1. $\mathbf{M}_3$ (not optimized) is also singular, but $\sum = 0.41$, a much lower value (this reminds one of the Heisenberg uncertainty principle: in $\mathbf{M}_1$ eight values are taken as 'exact,' and so the error necessarily accumulates in the last one). If the relative instead of the absolute errors are to be optimized, one could use weight factors.

RESULTS AND DISCUSSION

A case study was carried out by the author[15] on several compounds to compare the usefulness of the SVD, O/B and P–S approaches. Here, only some selected results for the compounds $Cp_3Pr \cdot \gamma Pic$ and $(MeCp)_3Ln \cdot \gamma Pic$ (Ln = Pr, Nd, Tm, Yb) are presented.

Computing geometry factors

The geometry of $Cp_3Pr \cdot \gamma Pic$ (Fig. 3) is known from x-ray analysis.[10] The G_i are easily found. To obtain geometry factors for the related compound $(MeCp)_3Pr \cdot \gamma Pic$, the bond lengths and angles shown as in Fig. 3 were adopted. The rest of the molecule was approximated by an idealized geometry [flat, regular rings, C—C single 154 pm, C—Cp center 121 pm, C—C(γPic ring) 137 pm, C—H 108 pm; see Ref. 15 for details]. The geometry factors of the γPic part of the molecule are the same as for $Cp_3Pr \cdot \gamma Pic$.

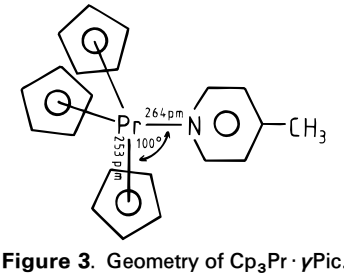

Figure 3. Geometry of $Cp_3Pr \cdot \gamma Pic$.

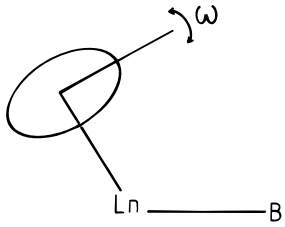

Figure 4. Definition of the libration angle ω (schematic).

Table 1. Geometry factors and hyperfine coupling parameters for $Cp_3Pr\cdot\gamma$Pic protons

Method	Pic-Me	Pic-α	Pic-β	Cp-H
	Geometry factor, G (10^{21} cm^{-3})			
XRAY	+4.98	+23.46	+8.91	−8.62
O/B	+4.98	+23.46	+8.34	−7.20
SVD	+4.98	+23.46	+8.91	−8.62
	Hyperfine coupling parameter, A (MHz)			
O/B	0	−0.02	+0.01	−0.19
SVD	+0.01	+0.01	+0.06	−0.28

Table 2. Geometry factors and hyperfine coupling parameters for $(MeCp)_3Pr\cdot\gamma$Pic protons

Method	Pic-Me	Pic-α	Pic-β	Cp-α	Cp-β	Cp-Me
	Geometry factor, G (10^{21} cm^{-3})					
XRAY	+4.98	+23.46	+8.92	−7.60	−5.21	(−5.70)
O/B	+4.98	+23.46	+8.13	−7.42	−5.01	(+4.52)[a]
SVD	+4.97	+23.46	+8.90	−7.62	−5.22	(+10.1)[a]
	Hyperfine coupling parameter, A (MHz)					
O/B	0	+0.04	+0.01	−0.05	−0.04	—[b]
SVD	−0.01	−0.01	+0.04	−0.02	−0.02	—[b]

[a] Extrapolated value.
[b] Not computed; see Ref. 15 for details.

Table 3. Geometry factors, G (10^{21} cm^{-3}), for $(MeCp)_3Nd\cdot\gamma$Pic protons

Method	Pic-Me	Pic-α	Pic-β	Cp-α	Cp-β	Cp-Me
XRAY	+5.00	+23.41	+8.95	−7.51	−5.11	(−5.70)[a]
O/B	+5.00	+23.41	+9.5	+61.7	+70.1	(−38.1)
SVD	+5.00	+23.41	+8.95	−7.51	−5.11	—[b]

[a] Value for Pr.
[b] Not computed; see Ref. 15 for details.

Table 4. Hyperfine coupling parameters, A (MHz), for $(MeCp)_3Ln\cdot\gamma$Pic protons

Lanthanoid	Pic-Me	Pic-α	Pic-β	Cp-α	Cp-β	Cp-Me
Pr	−0.01	−0.01	+0.04	−0.02	−0.02	—[a]
Nd	−0.01	+0.05	+0.03	−0.15	−0.15	—[a]
Tm	−0.02	−0.26	−0.04	+0.38	+0.16	—[a]
Yb	+0.05	−0.13	+0.04	+0.64	+1.02	—[a]
P/S value	0	+1.37	+0.30	−1.77	−1.77	+0.58

[a] Not computed; see Ref. 15 for details.

For the Cp ring a complication arises: it is *a priori* not known how the ring would rotate on the NMR time-scale. Molecular models suggest that the methyl groups would affect themselves most when located in a transoid orientation to the γPic ring. Therefore, a libration angle ω (Fig. 4) was defined. The geometry factors for all possibilities from $\omega = 0°$ (frozen rotation) to $\omega = \pm 180°$ (free rotation) were computed in steps of 10°. The best fit computed[15] with the O/B method (and confirmed by SVD) occurred for $\omega = \pm 120°$. This value is used below.

As, moreover, the wavefunctions of the crystal field states of the similar compound $Cp_3Pr\cdot MeTHF$ (the optical spectra are nearly identical) are known in detail,[5] D and X can be computed. Therefore, these compounds are ideally suited for a critical comparison of the O/B, P–S and SVD approaches.

$Cp_3Pr\cdot\gamma$Pic

In Table 1, the geometry factors calculated[15] via the structure parameters ('XRAY'), by the O/B and SVD methods are compared. The G_i values obtained by the O/B method are fairly good. The 'error redistribution' effect of SVD is most pronounced; the G_i are identical. One should keep in mind that this proves only the self-consistency, and not that the G_i are the 'right' ones. (Of course, even SVD could not fit random G values, so it can be concluded that these computed G values are 'close' to the correct ones; see below.)

Additionally, the calculated hyperfine coupling parameters are given. The difference between the O/B and SVD values is fairly large. It is most instructive to repeat this calculation with a slightly different set of geometry factors: even using SVD, the computed A_i vary widely.[15] After what was said in the earlier sections, this is not surprising.

Moreover, for some similar compounds of the type $Cp_3Pr\cdot B$ the hyperfine coupling parameter of the Cp proton as computed[21] by SVD took values around -0.20 MHz, with individual differences of nearly ± 0.10 MHz. This error margin would be hard to improve.

$(MeCp)_3Pr\cdot\gamma$Pic (Table 2)

The same computations were made as for $Cp_3Pr\cdot\gamma$Pic. Again, the O/B values for the G_i are acceptable and the SVD values are very good. The Cp ring methyl proton is a special case. There are too many degrees of freedom, and steric hindrances are possible, so the G_i computed from the structural parameters is not reliable. Including that value in the fit would lead to an error explosion even for SVD, and the 'true' G value probably lies in the direction indicated by SVD.

$(MeCp)_3Nd\cdot\gamma$Pic (Table 3)

This is an example where O/B completely fails. (Choosing values of the libration angle other than $\omega = \pm 120°$ does not affect this, the predicted G_i values are completely out of range.) As was pointed out earlier, this is just a numerical 'accident' (using the slightly

Table 5. Isotropic shifts (ppm) *vs.* temperature, *T* (K)

Compound	*T*	300	290	280	270	260	250	241	231	221	212			
$Cp_3Pr \cdot \gamma Pic$	Pic-Me	11.1	11.7	12.3	13.0	13.7	14.5	15.3	16.2	17.2	18.1			
	Pic-α	53.2	56.0	59.1	62.1	65.7	69.5	73.0	77.4	82.1	86.4			
	Pic-β	18.0	19.0	20.1	21.1	22.4	23.7	24.9	26.4	28.0	29.5			
	Cp-H	−7.3	−7.9	−8.5	−9.1	−9.8	−10.7	−11.4	−12.3	−13.3	−14.2			
	T	310	301	291	281	272	262	253	243	234	224	215	205	201
$(MeCp)_3Pr \cdot \gamma Pic$	Pic-Me	11.1	11.7	12.3	12.9	13.5	14.2	14.9	15.7	16.6	17.5	18.5	19.7	20.3
	Pic-α	50.6	53.3	56.1	59.1	61.8	65.2	69.0	73.0	77.7	82.5	87.6	92.9	95.8
	Pic-β	17.9	18.9	19.8	20.9	21.8	22.9	24.2	25.5	27.0	28.6	30.2	32.2	33.3
	Cp-α	−13.9	−14.9	−16.0	−17.1	−18.2	−19.5	−20.9	−22.4	−24.1	−25.8	−27.6	−29.6	−30.7
	Cp-β	−9.4	−10.1	−10.8	−11.6	−12.3	−13.2	−14.1	−15.1	−16.2	−17.4	−18.7	−20.0	−20.7
	Cp-Me	8.1	8.7	9.4	10.1	10.8	11.6	12.5	13.5	14.5	15.6	16.8	18.0	18.7
	T	310	301	291	281	272	262	253	243	234	224	215	205	195
$(MeCp)_3Nd \cdot \gamma Pic$	Pic-Me	7.2	7.5	7.9	8.2	8.6	9.0	9.5	9.9	10.4	10.9	11.7	12.5	13.1
	Pic-α	27.9	29.3	30.7	32.3	33.9	35.6	37.6	39.4	41.3	43.4	45.9	48.4	50.9
	Pic-β	10.2	10.7	11.2	11.7	12.3	12.9	13.6	14.2	15.0	15.9	16.6	17.4	18.6
	Cp-α	−0.6	−0.9	−1.1	−1.3	−1.7	−2.1	−2.4	−2.7	−3.1	−3.4	−3.9	−4.4	−4.9
	Cp-β	2.6	2.5	2.4	2.3	2.2	2.0	1.9	1.8	1.6	1.5	1.2	0.9	0.6
	Cp-Me	2.9	3.1	3.4	3.7	4.1	4.4	4.8	5.2	5.6	6.1	6.6	7.1	7.6
	T	310	262	253	243	234	224	215	205					
$(MeCp)_3Tm \cdot \gamma Pic$	Pic-Me	−36.5	−43.6	−46.1	−48.1	−50.6	−52.6	−55.0	−57.6					
	Pic-α	−185.6	−224.5	−235.5	−245.5	−257.5	−269.5	−282.5	−296.5					
	Pic-β	−66.2	−78.7	−82.4	−85.9	−89.7	−93.7	−97.7	−102.3					
	Cp-α	92.0	118.2	124.6	131.4	139.2	147.1	155.7	165.6					
	Cp-β	76.5	88.9	92.8	96.7	101.0	104.9	108.8	112.8					
	Cp-Me	−47.0	−61.9	−65.8	−70.0	−74.2	−79.0	−83.8	−89.3					
	T	310	301	291	281	272	262	253	243	234				
$(MeCp)_3Yb \cdot \gamma Pic$	Pic-Me	−21.3	−22.5	−23.8	−25.1	−26.2	−27.7	−28.9	−30.3	−32.0				
	Pic-α	−108	−114	−120	−126	−132	−138	−144	−151	−160				
	Pic-β	−39.3	−41.6	−44.0	−46.4	−48.7	−51.0	−53.4	−56.2	−58.9				
	Cp-α	57.4	59.8	62.7	65.4	68.0	71.0	74.5	77.9	82.8				
	Cp-β	71.3	73.5	76.4	79.0	82.4	85.8	90.7	95.5	99.9				
	Cp-Me	−32.4	−33.6	−35.1	−36.5	−38.3	−40.2	−42.1	−44.3	−46.6				

modified version of O/B already gives a fit comparable to the homologous Pr compound[15]), and SVD reproduces the G_i without any problems.

Evaluating P/S

In Table 4, the hyperfine coupling parameters for the homologous lanthanoid series $(MeCp)_3Ln \cdot \gamma Pic$ (Ln = Pr, Nd, Tm, Yb) computed by SVD are compared with the value predicted by P/S as given by Breitbach.[10] Note that only Pr and Nd ($\omega = \pm 120°$) and Tm and Yb ($\omega = \pm 180°$) are directly comparable, because for the latter the O/B method (and SVD) suggested a different optimum value of the libration angle ω. (The values are counter-intuitive, as considering the effect of lanthanide contraction would suggest exactly the opposite behaviour; see Ref. 15 for a further discussion.)

The values of the A_i predicted by SVD clearly contradict the P/S postulate. Moreover, the magnitude of the P/S values seem to be unrealistically high. However, in view of the large error margin (take $\pm 50\%$ for safety), the final verdict should be arrived at using a method that could access the A_i values more directly, such as that outlined in the section Unexplored ideas.

OUTLOOK

Most urgently needed now are precise experimental data to investigate the limits of the SVD approach, especially regarding the computation of reliable hyperfine coupling parameters. Here independent EPR or ENDOR data would be most valuable. Anyway, the research field still leaves enough open questions for work to continue.

EXPERIMENTAL

As this work attempted a critical re-analysis of known experimental results, no experiments of our own were carried out. The raw isotropic shift data for the compounds analyzed here are collected in Table 5. Further details can be found in Refs 9, 10 and 15.

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REFERENCES

1. J. W. Longley, *Least Squares Computations Using Orthogonalization Methods*, *Lecture Notes in Pure and Applied Mathematics*, No. 93. Marcel Dekker, New York (1984).
2. T. P. E. Auf der Heyde, *J. Chem. Educ.* **67**, 461 (1990).
3. H. Barkhuijsen, R. deBeer, W. M. M. J. Bovee and D. van Ormondt, *J. Magn. Reson.* **61**, 465 (1985).
4. K. G. Orrell, *Annu. Rep. NMR Spectrosc.* **9**, 1 (1979).
5. R. E. Sievers (Ed.), *NMR Shift Reagents*. Academic Press, New York (1973).
6. A. M. Grotens, J. J. M. Backus and E. de Boer, *Tetrahedron Lett.* 4343 (1973).
7. A. A. Chalmers and K. G. R. Pachler, *J. Chem. Soc., Perkin Trans. 2* , 748 (1974).
8. S. Spiliadis and A. A. Pinkerton, *J. Chem. Soc., Dalton Trans.* 1815 (1982).
9. W. Oroschin, PhD Thesis, University of Hamburg (1986).
10. H. Breitbach, PhD Thesis, University of Hamburg (1987).
11. C. N. Reilly, B. W. Good and J. F. Desreux, *Anal. Chem.* **47**, 2110 (1975).
12. C. N. Reilly, B. W. Good and R. D. Allendoerfer, *Anal. Chem.* **48**, 1446 (1976).
13. P. C. M. van Zijl, R. P. van Wezel, C. MacLean and A. A. Bothner-By, *J. Phys. Chem.* **89**, 204 (1985).
14. J. W. M. de Boer, P. J. D. Sakkers, C. W. Hibbers and E. de Boer, *J. Magn. Reson.* **25**, 455 (1977).
15. H. Reddmann, PhD Thesis, University of Hamburg (1993).
16. R. J. Kurland and B. R. McGarvey, *J. Magn. Reson.* **2**, 286 (1970).
17. B. Bleaney, *J. Magn. Reson.* **8**, 91 (1972).
18. B. R. McGarvey, in *Organometallics of the f-Elements*, edited by T. J. Marks and R. D. Fischer, p. 323. Reidel, Dordrecht (1978).
19. O. A. Gansow, P. A. Loeffler, R. E. Davis, R. E. Lenkinski and M. R. Willcott, III, *J. Am. Chem. Soc.* **98**, 4250 (1976).
20. M. F. Richardson, S. M. Rothstein and W. K. Li, *J. Magn. Reson.* **36**, 69 (1979).
21. H. Schulz, PhD Thesis, University of Hamburg (1994).

