2.60 (m, 3H); IR(film) 1710 cm^{-1}. 1-Adamantyl n-butyl ketone: NMR($CDCl_3$)δ 0.70 - 2.20 (m, 22H), 2.40 (d, 2H, J = 6 Hz); IR(film) 1710 cm^{-1}. n-Butyl mesitoyl ketone: NMR ($CDCl_3$)δ 0.70 - 2.20 (m, 7H), 2.17 (s, 6H), 2.25 (s, 3H), 2.65 (t, 3H, J = 6 Hz), 6.83 (s, 2H); IR(film) 1695 cm^{-1}. 11-Oxo-1-pentadecene: NMR($CDCl_3$)δ 0.76 - 1.10 (m, 1H), 1.10 - 2.60 (m, 22H), 4.80 - 6.20 (m, 3H); IR(film) 1715 cm^{-1}. Methyl 6-oxodecanoate: NMR($CDCl_3$)δ 0.70 - 1.10 (m, 3H), 1.10 - 2.10 (m, 8H), 2.10 - 2.80 (m, 6H), 3.70 (s, 3H); IR(film) 1740, 1720 cm^{-1}. β-Phenyl heptanophenone: NMR($CDCl_3$)δ 0.80 - 1.30 (m, 3H), 1.30 - 2.80 (m, 15H); IR(film) 1715 cm^{-1}. 4-Phenyl-2-octanone: NMR($CDCl_3$)δ 0.65 - 1.95 (m, 9H), 2.00 (s, 3H), 2.65 - 2.80 (d, 2H, J = 7 Hz), 2.80 - 3.40 (m, 1H), 7.30 (s, 5H); IR(film) 1715 cm^{-1}. 3-n-Butyl-1-cyclohexanone: NMR ($CDCl_3$)δ 0.80 - 1.30 (m, 3H), 1.30 - 2.80 (m, 15H); IR(film) 1715 cm^{-1}. 4,4-Dimethyl-3-n-butyl-1-cyclohexanone: NMR($CDCl_3$)δ 0.70 - 1.05 (m, 3H), 1.05 - 1.18 (d, 6H), 1.18 - 2.15 (m, 9H), 2.15 - 2.70 (m, 4H); IR(film) 1715 cm^{-1} 2,3-Dihydro-3-n-butylcarvone: NMR($CDCl_3$)δ 0.60 - 1.60 (m, 9H), 1.70 (s, 3H), 1.80 - 2.80 (m, 6H), 4.70 (m, 2H); IR(film) 1715 cm^{-1} 3-n-Butyl-3-methyl-5,5-dimethyl-1-cyclohexanone: NMR ($CDCl_3$)δ 0.90 - 1.10 (m, 3H), 1.22 (s, 9H), 1.30-1.62 (m, 6H), 1.70 (s, 2H), 2.35 (s, 4H); IR(film) 1715 cm^{-1}. 2-(1',1'-dimethylpentyl)-5-methyl-1-cyclohexanone: NMR($CDCl_3$)δ 0.70 - 1.50 (m, 18H), 1.50 - 2.66 (m, 8H); IR (film) 1715 cm^{-1}.

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Basis Set Requirement for Small Components Besides Kinetic Balance in Relativistic Self-Consistent-Field Calculations of Many Electron Systems

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It is demonstrated by using a highly positive uranium ion as a test case that the exact relation between the small and the large components of a Dirac spinor in relativistic self-consistent-field (RSCF) calculations is not fully satisfied by the kinetic balance condition only even for two electron systems. For a fixed number of large component basis functions, total energies are sensitive to the change of the size of the small component basis sets even after the kinetic balance condition is fully satisfied. However, the kinetic balance condition appears to be a reasonable guideline in generating reliable and practical basis sets for most applications of RSCF calculations. With a complete small component basis set, energies from RSCF calculations exhibit a variational behavior, implying the stability of the present RSCF procedure.

Introduction

The primary mechanism for variational failure in relativistic self-consistent-field (RSCF) calculation for one electron problems has been identified and practical and theoretical ways of obtaining variationally safe solutions have been derived recently by many workers. Schwarz and Wallmerer[1] have shown that an inadequate representation of the small component of the four-component Dirac spinor produces a shortfall in the computed kinetic energy, and that this persists even in the nonrelativistic limit ($c = 10^8$) where the small components might be expected to have negligible influence. This leads to

the idea of imposing 'kinetic balance' requirement in the basis set for RSCF calculations to obtain the correct nonrelativistic limit.

The importance of this kinetic balance has been mathematically analyzed by Grant *et. al.*[2] They also numerically showed using several kinds of basis functions[3] that the kinetic balance leads to stable upper bound of exact value for many Hydrogen-like atoms. The kinetic balance has also been the main subjects for other studies with all of them reaching the same conclusions.[4-7]

All the theoretical analyses available at present, however, are restricted to one electron systems. The concept obtained from the investigation of one electron systems has been used as a guideline in RSCF calculations for many-electron systems[5] without any further justification.

It is evident that the kinetic balance leads to correct nonrelativistic limit even for many-electron systems. The kinetic balance, however, may not be sufficient for correct relativistic calculations for many electron-system, especially when the relativistic effects are large, because obtaining the correct nonrelativistic limit does not necessarily guarantee correct relativistic calculations. But it should be noted that kinetic balance condition is the only useful guideline in selecting basis functions at present for any practical RSCF calculations.

For a given large component, there are other conditions to be satisfied by small component than just the kinetic balance. In the following sections, we present a probable origin for this additional requirement and numerical evidences supporting the present argument are shown by comparing results of RSCF calculations for two-electron uranium ion using various number of basis functions with the exect result obtained from atomic Dirac-Hartree-Fock (DHF) calculation.

In the numerical DHF calculations and RSCF calclations with complete basis sets, the problem of balance between small and large components is totally irrelevant since any relations between two components can be fully satisfied for these cases. However, these exact relativistic Hartree-Fock calculations are not feasible for general molecules and the understanding of basis set requirement in the finite basis set calculations is crucial for successful RSCF calculations for molecules.

Present test calculations indicate that the additional requirements other than kinetic balance are detactable but small enough to be neglected in most practical applications for basis sets of reasonable sizes.

Kinetic Balance and Exact Balance

For one electron atoms, the exponents of basis functions for large and small components of spinors must be equal as dictated by the kinetic balance condition.[2] For many electron systems, however, the exponents of basis functions for large components of spinors are not equal to those for small components, when exponents for basis functions are obtained by fitting to the numerical atomic spinors from Dirac-Hartree-Fock (DHF) calculation,[8] which are exact solutions, with disired number of Slater type functions. It is probable that the kinetic balancing is not the exact relation between large and small component spinor. We will examine in this section what the exact relation is, and how important the kinetic balance is from the point of exact relation.

For a single electron in an arbitrary potential V, the Dirac equation is as following,[9]

$$\begin{pmatrix} V\,I & c\,\alpha\cdot P \\ c\,\alpha\cdot P & (V-2c^2)I \end{pmatrix}\begin{pmatrix}\psi^L\\ \psi^S\end{pmatrix} = E\begin{pmatrix}\psi^L\\ \psi^S\end{pmatrix} \qquad (1)$$

Where α and I are 2×2 pauli and identity matrices, respectively, c refers to the speed of light, P to the momentum operator, E to the energy, ψ^L and ψ^S are large and small two component spinors, respectively.

From Eq.(1), an expression can be obtained for the small component spinor

$$\psi^S = \frac{1}{2c^2(1+(E-V)/(2c^2))}\,c\,\alpha\cdot P\,\psi^L \qquad (2)$$

This exact relation between the large and small component of spinor can be expanded as following,

$$\psi^S = \frac{1}{2c}\left[1-\frac{E-V}{2c^2}+\frac{(E-V)^2}{4c^4}-\frac{(E-V)^4}{8c^6}+\cdots\right]\alpha\cdot P\,\psi^L$$
$$= \left[\frac{1}{(2c^2+E)}+\frac{V}{(2c^2+E)^2}+\frac{V^2}{(2c^2+E)^3}\cdots\right]\alpha\cdot P\,\psi^L \qquad (3)$$

When $|V| << (2c^2+E)$ is satisfied, only the first term needs to be retained for a reasonable estimate of ψ^S from ψ^L. This is the condition called kinetic balance. In the nonrelativistic limit where the value of c becomes infinite, the kinetic balance is an exact relation between small and large component of a given spinor.

The radial part of the exact solution for the Dirac equation is a linear combinations of functions with exponential times nonintegar power of r, for example the H-like Dirac spinor.[10]

These functions with noninteger power of r, however, are inconvenient for molecular applications, and Slater type functions (STF's) with integer power of r are usually used in RSCF calculations,[5] because computation of integrals using STF's with noninteger power of r are much more diffcult and time consuming. When ψ^L and ψ^S are expanded using STF basis sets satisfying the kinetic balance condition, the exact relation is satisfied reasonably except near and at the nucleus for a Coulombic potential $V=(-Z/r)$. In the case of one electron atom, therefore, the kinetic balance condition is a good asymptote approximation of the exact relation, although it is still possible to obtain a spurious root as shown by Ishikawa, Baretty and Sando.[11] It is noted that the relation given by Eq.(3) requires the same value of exponents for large and small components regardless of the power of r in the basis functions.

In the case of many electron atoms, the potential V also contains electron interaction terms. In the Haree-Fock theory and thus in RSCF methods, the interaction potential for an electron is an average potential generated by rest of electrons. Since the analytical treatment of the many electron potential is not possible, we will examine a simple case for two electron atoms in the following using Eq.(3). Although DHF equations for spinors of two electron atoms[8] are different from Eq(3), the equation contains all the necessary features for the present analysis.

In the two electron atom, where both electrons occupy 1s shell, the electron repulsion part of the potential, V(2) can be written as

$$V(2) = 4\pi \left\{ \frac{1}{r_1} \int_0^{r_1} \phi_2^* \phi_2 \; r_2^2 dr_2 + \int_{r_1}^{\infty} \phi_2^* \phi_2 r_2 \, dr_2 \right\} \tag{4}$$

$$= \frac{\pi N^2}{r\zeta^3} - \frac{\pi N^2}{\zeta^3 r} \exp(-2\zeta r) - \frac{\pi N^2}{\zeta} \exp(-2\zeta r).$$

using the standard expansion for $1/r_{12}$ term.[10]

Assuming that the electron density represented by small components is small, density given by four component spinor, ψ, is reasonably approximated by using only the large components.

If one 1s STF is used for the large component spinor,

$$\psi^L(1) = N \exp(-\zeta r) \begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ and}$$

$$\psi^L(2) = N \exp(-\zeta r) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{5}$$

one can approximately evaluate the integral and obtain an expression for V(2) in terms of ζ. By adding nuclear attraction to V(2), the average potential for this simple case becomes

$$V = -\frac{Z}{r} + V(2)$$

$$= \frac{1}{r}\left[\frac{\pi N^2}{\zeta^2} - Z\right] - \frac{\pi N^2}{\zeta^3 r} \exp(-2\zeta r) - \frac{\pi N^2}{\zeta} \exp(-2\zeta r).$$

$$= \frac{C_1}{r} - \frac{C_2}{r} \exp(-2\zeta r) - C_3 \exp(-2\zeta r) \tag{6}$$

By substituting Eq.(6) into Eq.(3), it can be seen that the small component corresponding to the large component of Eq.(5) contains functions whose exponents are different from ζ.

These functions are not obtained from the kinetic balance condition. If only one exponent is also used in the expansion of small components, the optimal value for the exponent of small component basis function is slightly different from what is required by the kinetic balance condition. The actual value of optimal exponent for small components depends not only on the magnitude but also on the form of the second term in Eq.(3). Therefore the kinetic balance criterion in two electron case is a poorer approximation of the exact relation between large and small component than in the one electron case. It is expected that the argument made for a simple two electron atom here is also valid for general cases.

In order to investigate the effect of the electron interactions to the relation between large and small components of spinor, properties of different basis sets are tested in RSCF calculations for two electron uranium ion. U^{+90}. Results of these calculations and suggestions for selecting small component basis functions are given in the following sections.

Test Calcultions for a Two Electron Ion

In order to obtain a basis set for many-electron system, the numerical atomic spinors obtained by numerical DHF calculations[7] are fitted by a given number of Slater type functions. Non-linear least square technique is used in the fitting[12] and the size of basis set is determined by the number of functions used in the fitting. Because the numerical atomic spinors are the exact solutions of the DHF equation, it is expected that the basis set obtained by this method mimics exact relation of Eq.(3) better than that from kinetic balance condition. In the present test, the numerical atomic spinor for Uranium ion, U(+90), was fitted using n 1s STF's for large component and m 1p STF's for small component atomic spinor. The resultant exponents of these STF's are given in Table 1.

As can be expected from the discussion in the preceding section, the exponents of a small component basis set are not exactly equal to but slightly different from those of the corresponding large component basis. This is a numerical evidence that the kinetic balancing is not an exact relation between large and small components of spinors. But the dif-

Table 1. Exponents of Basis Functions Obtained by Fitting. nL and mS in the first Column Indicate that the Large Component Atomic Spinor is Fitted with n 1s-STP, and that the Small Component Atomic Spinor is fitted with m 1p-STP, Respectively

Basis nL,mS	Large component Exponents		Small component Exponents	
1L,1S	110.56963		110.78022	
2L,2S	353.23296 ;	101.48728	352.13155 ;	101.55428
3L,3S	1012.64610 ;	235.99400	1012.39530 ;	235.82958
	98.25600		98.28864	
4L,4S	2398.03600 ;	565.49869	2398.10460 ;	565.49203
	190.26169 ;	96.52602	190.50066 ;	96.54949
5L,5S	4626.29350 ;	1181.45520	4623.75270 ;	1180.65380
	398.17502 ;	164.71644	397.67432 ;	165.00936
	95.40576		95.42336	
6L,6S	7549.44180 ;	2149.49100	7544.74470 ;	2147.79710
	761.95068 ;	311.49590	761.25045 ;	310.83781
	148.42297 ;	94.625399	148.63116 ;	94.637335

Table 2. Calculated Relativistic Total Energies and 1S orbital Energies for U(+90), Using n-1s STP for the Large Component and m-1p STP for the Small Component of the Wavefunction in the Relativistic Calculations. Exponents of These n-1s and m-1p basis Functions are given in Table 1

Basis nL,mS		Total Energy in a.u.	Orbital Energy of 1s in a.u.
1L,1S	L≠S	-9578.87845	-4754.8789
	L=S	-9574.57259	-4752.7333
2L,2S	L≠S	-9642.25285	-4785.0520
	L=S	-9642.97931	-4785.4042
3L,3S	L≠S	-9649.86427	-4789.8043
	L=S	-9649.82028	-4789.7822
4L,4S	L≠S	-9650.95122	-4789.9512
	L=S	-9650.94844	-4789.9503
5L,5S	L≠S	-9651.18335	-4790.2413
	L=S	-9651.19004	-4790.2452
6L,6S	L≠S	-9651.26291	-4790.1936
	L=S	-9651.25996	-4790.1924
DHF calculation		-9651.39893	-4790.2906

Table 3. The Relativistic Kinetic Energies and the Potential Energies for each Basis set

Basis	kinetic energy		potential energy	
nL,mS	L#S	L=S	L#S	L=S
1L,1S	19023.2845	19029.3197	-20279.9844	-20275.7059
2L,2S	23260.0640	23277.8406	-22942.7222	-22955.0840
3L,3S	22427.4714	22427.4164	-22526.2238	-22526.0081
4L,4S	22727.7528	22727.2504	-22692.2712	-22691.9538
5L,5S	22619.9355	22619.7227	-22637.0790	-22636.9614
6L,6S	22674.4265	22674.1260	-22665.9590	-22665.7381

ferences seem to be quite small.

Relativistic SCF calculations for U(+90) using these basis sets were performed and the results are given in Table 2 for total energies, orbital energies, in Table 3 for total potential energies and total kinetic energies. Where L=S in second column means that the large component exponents given in Table 1 are used for both large and small component basis functions, satisfying the kinetic balancing, and L#S means that the slightly different exponents given in Table 1 are used for large and small component basis functions, approximately satisfying the exact relation.

The total energies and orbital energies obtained by basis set expansion method are always larger than the true total energy and orbital energy as shown in Table 2. The result of basis set expansion calculations approach the true value as the size of basis sets becomes large regardless of types of basis sets.

Total energies and orbital energies obtained using L#S basis are lower than those obtained using corresponding L=S basis except 2L,2S and 5L,5S as shown in Table 2. This reversal do not occur in the nonrelativistic limit calculations using these basis sets in RSCF calculations.

From the point of kinetic balancing, the results obtained using L#S basis may be interpreted as following. Because the kinetic balancing is not satisfied, the kinetic energy may be underestimated as discussed by Grant[3,4] and the total energy is lower than that obtained using L=S basis set. The relativistic kinetic energies, however, obtained using L#S basis sets are not lower than those using corresponding L=S basis sets except for 1L,1S and 2L,2S as given in Table 3. The potential energies, on the other hand, of L#S basis sets are lower than those of L=S basis sets except for 2L,2S.

This potential energy deficiency can make the total energies from fitted basis sets (L#S) higher than those from kinetically balanced basis sets (L=S). It should be noted that relativistic kinetic and potential energies are not exactly the kinetic and potential energies because relativistic corrections are also contained in these energies.[13]

Although this potential energy deficiency could also happen in H-like atom because of Z/r term in Eq.(6), the main reason of this phenomenon, we think, is the interaction between electrons. In the case of one electron the momentum operator $(\alpha \cdot p)$ is the only source connecting large component and small component of spinor. The rule of small component is important only for the kinetic energy calculation as analyzed by I.P. Grant.[3,4] The dependence of the potential energy on small component, on the other hand, is proportional to the square of the coefficients of small component which is very small compared to that of large component. Therefore, the dependence of the total potential energy on the small component of spinor in the one electron atom is negligible.

Table 4. Exponents of Seven basis Function. Exponents of Basis C and E are Obtained by Fitting the Large Component of the Numerical Atomic Spinor of U(+90) with two STF's, and the Exponents of Remaining basis Functions are Selected to Approximate the Complete Space

Basis	A	B	C	D	E	F	G
Exp	2500.0	900.0	353.23296	277.0	101.48728	67.0	31.0

Table 5. Result of Relativistic SCF Calculations for U(+90). The large Component wave Function is Expanded using two Basis Functions, but Sizes of the Small Component Basis set are Different. All energies are in Atomic Units

Basis nL,mS	Small component basis functions	Total energy	Orbital energy	(T/V)
DHF calculation		-9651.399	-4790.290	
2L,2S	C , E	-9642.991	-4785.410	-1.0140
2L,3S	C,D,E	-9602.260	-4765.563	-1.0030
2L,4S	B,C,D,E	-9567.167	-4748.386	-0.9986
2L,5S	B,C,D,E,F	-9566.328	-4747.976	-0.9987
2L,6S	A,B,C,D,E,F	-9566.256	-4747.940	-0.9987
2L,7S	A,B,C,D,E,F,G	-9566.142	-4747.885	-0.9987

In the case of two electron atom, however, the inter-electron repulsion term is an another source linking large and small components of spinors. This linkage may not be apparent in the Dirac equation, Eq.(1), because electron interaction term, V(2), occurs only in diagonal element of matrix equation. But V(2) are obtained from large and small components of spinors of other electrons.

For many electron systems, therefore, the kinetic balance is not sufficient, but the relation between large and small components of a spinor may be well approximated by the kinetic balance condition when the number of functions with the different value of exponents in the small components are restricted to be the same as that in the large components as is shown in the present result.

In order to properly evaluate the effect of the repulsive potential between electrons, more basis functions are required for small components than for the large components in Eq.(3).

Seven STF's, whose exponents are given in Table 4, are selected for basis sets of U(+90). Two of them, basis function C and E are obtained by fitting the large component of the numerical atomic spinor of U(+90) with two STF's, and the exponents of remaining basis functions are added to yield a reasonably complete description of 1S orbital space for U(+90).

Relativistic calculations for U(+90) have been performed using these basis sets. Total energies and orbital energies are calculated with the number of small component basis functions increasing from two to seven, but with the number of large component basis functions fixed as two, as indicated in the first column of Table 5.

Two functions with the same exponents (C and E) are us-

Table 6. Coefficients of two Basis Functions for the Large Component of Spinor

Basis	exp(−353.23296 r)	exp(−101.48728 r)
2L,2S	0.13397	0.84750
2L,3S	0.11721	0.86082
2L,4S	0.10902	0.86716
2L,5S	0.10897	0.86719
2L,6S	0.10896	0.86719
2L,7S	0.10895	0.86720

Table 7. Result of Relativistic SCF Calculations for U(+90). The small Component wave Function is Expanded using Seven Basis Functions, whose Exponents are A,B,C,D,E,F and G of Table 4, and the large Component wave Function is Expanded using Various number of Basis Function

Basis nL,mS	Large component basis functions	Total energy	Orbital energy	(T/V)
2L,7S	C , E	−9566.142	−4747.885	−0.9987
3L,7S	B,C, E	−9612.655	−4771.698	−0.9884
4L,7S	A,B,C, E	−9648.186	−4788.927	−0.9963
5L,7S	A,B,C,D,E	−9648.643	−4788.988	−0.9988
6L,7S	A,B,C,D,E,F,	−9648.644	−4788.983	−0.9989
7L,7S	A,B,C,D,E,F,G	−9649.017	−4789.147	−0.9992
DHF calculation		−9651.399	−4790.290	

ed for both large and small component spinor in order to guarantee the kinetic balancing. Additional functions, added only in the basis set of small component, does not break the achieved kinetic balance in the ordinary sense. As shown in Table 5, the total energies and the orbital energies increase and approach a certain limit as the size of the basis set for small components increases. The difference between this limit and the result of 2L,2S is probably the deficiency present in the result of the relativistic SCF calculation using 2L,2S with L=S.

This change of result is largely due to the change of the large component itself. The change of large component when the number of the basis functions for small component increase, is definitely shown in Table 6, where the variation of coefficients of large component basis functions is given. The coefficient of basis function with larger exponent (353.28296) decreases, and that with smaller exponent (101.48728) increases indicating that the spinor becomes diffuse as the number of basis functions for small component increases. This demonstrates that there is a converged limit of complete small component space for a given set of large component basis functions.

Although the relation for the small component given by Eq.(3) is fully satisfied in this limit, the quality of energy at this limit is not clear. It is possible that the complete small component basis set eliminates artificial lowering of energy reported by Ishikawa *et. al.*.[11] If this is the case, RSCF calculations may be more reasonable than what might be expected from the theoretical ground.

Next, the size of the basis set for the large component spinor is increased with the number of the small component basis functions fixed at seven and results are summarized in Table 7.

The total energies and the orbital energies decrease and steadily converge to true values as in the nonrelativistic case. If the small component space is complete, the energy from RSCF calculation seems to converge toward the true values monotonously from above at least for the ground state of two electron atoms. Whether the same behavior will be observed for more complex system is still an open question. But our limited experience suggests that the RSCF calculations are stable if $n = l$ STF's are allowed only in small component space and not in large component.

Values denoted as (T/V) in Table 5 and 7 are relativistic analog of virial ratio.[13] Although these values do not exactly represent the quality of the basis set employed, they are still useful for rough estimates of the basis set qualities.

Conclusions and Discussions

We have investigated the basis set selection in RSCF calculations for a two electron system. The kinetically balanced basis sets yield very reasonable total energy and orbital energies, although it can be shown that the kinetic balance criterion is not sufficient for the exact relation between large and small component of spinors. Although the kinetic balance criterion always ensures that the kinetic energy is not underestimated, the possibility of underestimating the potential energy (overestimating in absolute magnitude) still remains as shown in the previous section. Since the differences between small components from the kinetic balance and those from fitting for DHF spinors are minor, the kinetic balance criteria can be used in generating small component basis sets for a given large component basis set for most purpose.

The basis sets satisfying just the kinetic balance can yield the energy below the true value especially for $j = l - 1/2$ shells with $l > 0$ even in the hydrogenic atoms.[11] Our experience suggests that this can probably be avoided by employing complete small component basis sets. Since the kinetically balanced small component basis set for many electron atoms contains fairly large number of functions, this spurious result may not invalidate RSCF calculations for many electron systems. This is just a speculation and the numerical experiments as well as the theoretical investigations are under way.

Given the prescription of kinetic balance for the small components, selection of large component basis set is a major prerequisite for an efficient and reliable RSCF calculations. Practical ways of optimizing large component basis sets are discussed elsewhere.[14]

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Contact-Only and Dipolar-Only Mixtures of Lanthanide NMR Shift Reagents

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Two new types of NMR shift reagents, one giving dipolar-only and the other giving contact-only shifts, can be prepared simply by mixing two appropriate Ln(fod)$_3$(Ln = Pr, Nd, Eu, and Yb) reagents in certain ratios. The ^{1}H and ^{13}C NMR spectra of pyridine-type substrates, quinoline and isoquinoline, whose paramagnetic shifts are normally a composite of contact and dipolar contributions with single lanthanide shift reagents, show the feasibility of this approach.

Introduction

Considerable interest has recently been shown in ^{1}H and ^{13}C NMR shifts, induced in a wide range of organic molecules by the lanthanide shift reagents.[1,2] These induced shifts $\Delta\delta_{ij}$'s are a combination of dipolar (or pseudocontact) and contact shifts caused by coordination of the organic molecule to the lanthanide shift reagent, according to eq. 1[3]

$$\Delta\delta_{ij} = G_i C_j^p + F_i \langle Sz \rangle_j \quad (1)$$

where C_j^p and $\langle Sz \rangle_j$ depend upon the lanthanide ion j being used and have been calculated by Bleaney[4,5] and Golding.[6,7] G_i and F_i depend upon the geometric location and electron spin density of the substrate nucleus i, respectively.

In the previous work[8] we demonstrated the applicability of contact-only and dipolar-only mixtures of the lanthanide shift reagents whose effective net C^p or $\langle Sz \rangle$ values were zero, to determine F_i and G_i values of the nuclei in 4-picoline. The F_i and G_i values obtained directly by the contact-only and the dipolar-only reagents, which were appropriate mixtures of Pr(fod)$_3$ and Eu(fod)$_3$, agreed well with those values obtained by experiments using individual Ln(fod)$_3$ reagents. But F_i and G_i values obtained directly by the contact-only and the dipolar-only reagents, which were mixtures of Nd(fod)$_3$ and Yb(fod)$_3$, deviated from the expected values. It was supposed that the deviation was due to the behavior of the ytterbium complex.

We report here the applicability of contact-only and dipolar-only mixtures of lanthanide shift reagents to determine F_i and G_i values for more complicate pyridine-type substrates (quinoline and isoqunoline), which provide informations about electron spin densities and geometries.

Table 1. Mole Ratios of Ln(fod)$_3$ for Contact-only (COM) and for Dipolar-only (DOM) Mixtures[a]

mixture	mole ratio		net $\langle Sz \rangle$	net C^p
	Eu(fod)$_3$/Pr(fod)$_3$	Yb(fod)$_3$/Nd(fod)$_3$		
COM 1	2.75	—	-7.04	0
COM 2	—	0.191	3.36	0
DOM 1	0.278	—	0	-7.73
DOM 2	—	1.73	0	12.4

[a] Computed from Bleaney's data(5) scaled to Dy value and from Golding's data (6) scaled to -100 for Dy.

Experimental

Materials. The substrates, quinoline and isoquinoline were purchased from Aldrich Chemical Co., distilled, and stored over Molecular Sieve 4A. The lanthanide shift reagents, Ln(fod)$_3$(Ln = Pr, Eu, and Yb; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) were commercial chemicals from Norell Inc. Nd(fod)$_3$ were synthesized as described by Sievers *et al.*[9] Contact-only and dipolar-only lanthanide shift reagents were prepared as described in the previous work.[8] Table 1 shows the mole ratios of Ln(fod)$_3$ used to prepare contact-only (COM 1 and COM 2) and dipolar-only (DOM 1 and DOM 2) reagents.

NMR Spectra. ^{1}H and ^{13}C NMR spectra were obtained