Reprinted from:

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 57, NUMBER 3 1 AUGUST 1972

Calculation of the Anisotropic Hyperfine Coupling in Cu(II) Bis(dithiocarbamate) and Cu(II) Bis(diselenocarbamate). A Formula for the Anisotropic Hyperfine Coupling Tensor

C. P. KEIJZERS AND E. DE BOER

Department of Physical Chemistry, University of Nijmegen, Nijmegen, The Netherlands

(Received 12 April 1972)

For a molecule with one unpaired electron a general formula is derived for the elements of the anisotropic hyperfine coupling tensor, taking into account all possible electron excitations. For a check of the formula the hyperfine coupling tensors are calculated for the copper atom in bis(N,N-diethyl dithiocarbamato) copper(II) and for the copper and selenium atoms in bis(N,N-diethyldiselenocarbamato) copper(II), using the iterative extended Hückel method. Both the calculated principal values of these tensors and the direction cosines of the principal axes are in good agreement with the experimentally observed ones.

I. INTRODUCTION

Already in 1958 Maki and McGarvey[1] expressed the spin Hamiltonian parameters in terms of atomic orbital coefficients of molecular orbital wavefunctions, describing an unpaired electron in a transition-metal complex. By experimental determination of the spin Hamiltonian they got expressions for the molecular orbital (MO) wavefunctions.

This procedure necessitates either a high symmetry of the molecule studied,[2] or a strong simplification of the expressions for the spin Hamiltonian parameters.[1,3]

In a previous paper[4] we showed that these simplifications are not allowed for g-value calculations. In this paper a general formula is derived for the elements of the anisotropic hyperfine coupling tensor. We show which excited states contribute and which do not. The resulting formula has been applied to the calculation of central atom and ligand hyperfine couplings in bis(N,N-diethyldithiocarbamato) copper(II) and bis(N,N-diethyldiselenocarbamato) copper(II), yielding values which are in very good agreement with the experimentally observed ones.

II. DEFINING THE PROBLEM

The system under consideration is a molecule containing N nuclei and $2n+1$ electrons, one of the electrons is unpaired. With the aid of second order perturbation theory, the hyperfine coupling of the electronic spin $\mathbf{S}$ with the spin $\mathbf{I}$ of the nucleus T will be calculated. The perturbing Hamiltonian is[5]:

$$\mathcal{H}_{\text{pert}}=\sum_i \{\mathcal{H}_{LS}{}^i+\mathcal{H}_{IL}{}^i+\mathcal{H}_{DD}{}^i\}, \tag{1a}$$

where the summation i runs over all electrons, and where

$$\mathcal{H}_{LS}{}^i=\sum_k \zeta(r_{ki})\mathbf{L}^{ki}\cdot\mathbf{S}^i, \tag{1b}$$

with $\zeta(r_{ki})$ being the one-electron spin–orbit coupling operator, and $\mathbf{L}^{ki}$ the angular momentum of the ith electron around the nucleus k. The summation k runs over all nuclei. The dipolar operator is

$$\mathcal{H}_{DD}{}^i=(P/r_i{}^3)\{[3(\mathbf{r}_i\cdot\mathbf{S}^i)(\mathbf{r}_i\cdot\mathbf{I})/r_i{}^2]-\mathbf{I}\cdot\mathbf{S}^i\}, \tag{1c}$$

with $P=g_e\beta_e g_T\beta_N$, g_e being the free electron g value, β_e the Bohr magneton, g_T the g value of the nucleus T, and β_N the nuclear magneton. The radius vector from the nucleus T towards the electron i is $\mathbf{r}_i$. Also,

$$\mathcal{H}_{IL}{}^i=(P/r_i{}^3)\mathbf{I}\cdot\mathbf{L}^i, \tag{1d}$$

where $\mathbf{L}^i$ is the angular momentum of the ith electron around the nucleus T. The dipolar operator $\mathcal{H}_{DD}{}^i$ may

TABLE I. Experimentally determined[a] and calculated values for Δg_{ii}, A_{ii}[b,c] and a_{iso}[b,d] for Cu(II)(N,N-diethyl dithiocarbamate)$_2$ doped in the corresponding Ni(II) complex.

	Obs	Calc	Cu	Obs	Calc
Δg_{xx}	0.0177±0.0010	0.0183	A_{xx}	43.0±2.8	40.5
Δg_{yy}	0.0227±0.0010	0.0227	A_{yy}	37.0±2.8	39.5
Δg_{zz}	0.0817±0.005	0.0767	A_{zz}	−80.0±1.6	−80.0
			a_{iso}	−79.0±1.2	

[a] Values obtained from M. J. Weeks and J. P. Fackler, Inorg. Chem. 7, 2548 (1968).

[b] Values for A_{ii} and a_{iso} in 10^{-4} cm^{-1}.

[c] A_{ii} are the principal values of the traceless A tensor.

[d] a_{iso} is the mean of the principal values of the nontraceless A tensor.

be rewritten as

$$\mathcal{H}_{DD}{}^i=(P/r_i{}^3)(4\pi/5)^{1/2}[I_xS_x{}^i(\sqrt{3}Z_{x^2-y^2}-Z_{z^2})^i+I_yS_y{}^i(-\sqrt{3}Z_{x^2-y^2}-Z_{z^2})^i+I_zS_z{}^i(2Z_{z^2})^i+(I_yS_x{}^i+I_xS_y{}^i)(\sqrt{3}Z_{xy})^i+(I_zS_x{}^i+I_xS_z{}^i)\times(\sqrt{3}Z_{xz})^i+(I_zS_y{}^i+I_yS_z{}^i)(\sqrt{3}Z_{yz})^i] \tag{2a}$$

$$=(P/r_i{}^3)\sum_{r,s=x,y,z} I_rS_s{}^iF_{rs}{}^i, \tag{2b}$$

where each Z function is a normalized real combination of spherical harmonics $Y_{2,m}$, centered on the nucleus T. By equating (2a) and (2b), the definition of $F_{rs}{}^{i}$ is obvious.

Because $\mathcal{H}_{\text{pert}}$ contains only one-electron operators, all states with two or more excited electrons do not contribute to the perturbation energy.

For the eigenfunctions $\Psi_n{}^{\sigma}$ of the unperturbed Hamiltonian, antisymmetrized functions are taken, consisting of one or more Slater determinants. The upper index of Ψ is the expectation value of S_z with respect to this function, the lower denotes the type of function. The Slater determinants are composed of one-electron spin orbitals $\psi\sigma(i)$. The spatial part ψ of a spin orbital is a MO consisting of a linear combination of atomic orbitals ϕ.

Omitting a normalization factor $N=\{(2n+1)!\}^{-1/2}$, the unperturbed functions of the ground and excited states are:

(a) Ground state,

$$\Psi_0{}^{\sigma}=|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_n\alpha(2n-1)\psi_n\beta(2n)\psi_{n+1}\sigma(2n+1)|.$$

(b) Excited states with an electron excited towards the MO of the unpaired electron,

$$\Psi_l{}^{\sigma}=|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\alpha(2n)\psi_{n+1}\beta(2n+1)|,\qquad l<n+1.$$

(c) Excited states with the unpaired electron excited towards an initially empty MO,

$$\Psi_h{}^{\sigma}=|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_n\alpha(2n-1)\psi_n\beta(2n)\psi_h\sigma(2n+1)|,\qquad h>n+1.$$

(d) Excited states with an electron excited from a doubly occupied MO towards an empty one. These excitations give rise to two doublet and one quartet state,

$$\Psi_{d_1}{}^{\sigma}=2^{-1/2}\{|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma'(2n+1)|$$
$$-|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma'(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma(2n+1)|\},\qquad l<n+1,\qquad h>n+1,\qquad \sigma\neq\sigma',$$

$$\Psi_{d_2}{}^{\sigma}=6^{-1/2}\{2|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma'(2n)\psi_h\sigma(2n+1)|$$
$$-|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma'(2n+1)|$$
$$-|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma'(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma(2n+1)|\},\qquad l<n+1,\qquad h>n+1,\qquad \sigma\neq\sigma',$$

$$\Psi_q{}^{\sigma}=3^{-1/2}\{|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma'(2n)\psi_h\sigma(2n+1)|$$
$$+|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma'(2n+1)|$$
$$+|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma'(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma(2n+1)|\},\qquad l<n+1,\qquad h>n+1,\qquad \sigma\neq\sigma',$$

$$\Psi_q{}^{3\sigma}=|\psi_1\alpha(1)\psi_1\beta(2)\cdots\psi_l\sigma(2l-1)\cdots\psi_{n+1}\sigma(2n)\psi_h\sigma(2n+1)|,\qquad l<n+1,\qquad h>n+1.$$

III. THE HYPERFINE COUPLING TENSOR

Defining a spin-Hamiltonian $\mathcal{H}_s=\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$, with $\mathbf{A}$ being the anisotropic hyperfine coupling tensor, we require $\mathcal{H}_s$ and $\mathcal{H}_{\text{pert}}$ to yield the same perturbation energy. Applying second order perturbation theory for degenerate states, the requirement is

$$\langle\Psi_0{}^{\sigma}\pi|\mathcal{H}_s|\Psi_0{}^{\sigma'}\pi'\rangle=\langle\Psi_0{}^{\sigma}\pi|\mathcal{H}_{\text{pert}}|\Psi_0{}^{\sigma'}\pi'\rangle+\sum_{n\neq0}\sum_{\sigma''}\sum_{\pi''}\langle\Psi_0{}^{\sigma}\pi|\mathcal{H}_{\text{pert}}|\Psi_n{}^{\sigma''}\pi''\rangle\langle\Psi_n{}^{\sigma''}\pi''|\mathcal{H}_{\text{pert}}|\Psi_0{}^{\sigma'}\pi'\rangle/(E_0-E_n),\tag{3}$$

where σ and σ' and the nuclear spin functions π and π' are arbitrary and may be equal. The summations run over all possible excited states, E_0-E_n being the excitation energy.

A. First Order Contribution

$\mathcal{H}_{LS}$ and $\mathcal{H}_{IL}$ do not contribute in first order. $\mathcal{H}_{DD}$ yields a traceless, symmetric tensor with elements

$$A_{vw}{}^{1}=P\langle\psi_{n+1}|F_{vw}/r^3|\psi_{n+1}\rangle,\tag{4}$$

where the symbols v and w are x, y, or z.

B. Second Order Contribution

In second order all terms are neglected which explicitly contain $\langle r^{-3}\rangle$ twice. The energies of the states are calculated by summing one-electron MO energies. The remaining terms have the form

$$\langle\Psi_0{}^{\sigma}\pi|\mathcal{H}_{IL}|\Psi_n{}^{\sigma''}\pi''\rangle\langle\Psi_n{}^{\sigma''}\pi''|\mathcal{H}_{LS}|\Psi_0{}^{\sigma'}\pi'\rangle\tag{5a}$$

and

$$\langle\Psi_0{}^{\sigma}\pi \mid \mathcal{H}_{DD} \mid \Psi_n{}^{\sigma''}\pi''\rangle\langle\Psi_n{}^{\sigma''}\pi'' \mid \mathcal{H}_{LS} \mid \Psi_0{}^{\sigma'}\pi'\rangle \tag{5b}$$

and the similar products with the operators interchanged.

It may be deduced that second order contributions from terms of the type (5a) yield a nontraceless tensor

$$A_{vw}{}^{2a}=2P\sum_{m\neq n+1}(E_{\psi_{n+1}}-E_{\psi_m})^{-1}\sum_{k=1}^{N}\langle\psi_{n+1}\mid\zeta(r_k)L_v{}^k\mid\psi_m\rangle\langle\psi_m\mid L_w/r^3\mid\psi_{n+1}\rangle, \tag{6}$$

where $L_v{}^k$ is the vth component of the angular momentum operator L^k centered on the nucleus k.

This contribution is due to excited states $\Psi_l{}^{\sigma}$ and $\Psi_h{}^{\sigma}$; the other excited states do not contribute.

Also the terms (5b) give a contribution which is due only to the excited states $\Psi_l{}^{\sigma}$ and $\Psi_h{}^{\sigma}$

$$A_{vw}{}^{2b}=P\sum_{m\neq n+1}\sum_{k=1}^{N}\sum_{u,t}[i\epsilon_{utv}/(E_{\psi_{n+1}}-E_{\psi_m})]\langle\psi_{n+1}\mid\zeta(r_k)L_u{}^k\mid\psi_m\rangle\langle\psi_m\mid F_{tw}/r^3\mid\psi_{n+1}\rangle, \tag{7}$$

with ϵ being the Levi–Civita symbol. The summations u and t run over the Cartesian coordinates x, y, and z.

The excited states $\Psi_{d_1}{}^{\sigma}$ do not give a contribution, while the contributions from the states $\Psi_{d_2}{}^{\sigma}$, $\Psi_q{}^{3\sigma}$, and $\Psi_q{}^{\sigma}$ cancel each other.

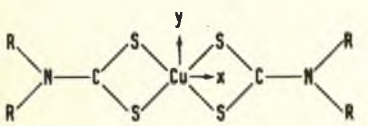
Summing up, the expression for a general tensor element is:

$$A_{vw}=P[\langle\psi_{n+1}\mid F_{vw}/r^3\mid\psi_{n+1}\rangle+\sum_{m\neq n+1}(E_{\psi_{n+1}}-E_{\psi_m})^{-1}\sum_{k=1}^{N}\{2\langle\psi_{n+1}\mid\zeta(r_k)L_v{}^k\mid\psi_m\rangle \times\langle\psi_m\mid L_w/r^3\mid\psi_{n+1}\rangle+\sum_{u,t}i\epsilon_{utv}\langle\psi_{n+1}\mid\zeta(r_k)L_u{}^k\mid\psi_m\rangle\langle\psi_m\mid F_{tw}/r^3\mid\psi_{n+1}\rangle\}]. \tag{8}$$

IV. APPLICATIONS

A. Cu(II)(*N*,*N*-Diethyldithiocarbamate)$_2$; Cu(dtc)$_2$

As is reported elsewhere,[4] we performed iterative extended Hückel calculations on the compound



R = ethyl

taking into account all valence orbitals. Using the structure of the host lattice [that is the corresponding Ni(II) complex[6]] and employing values for the empirical parameters which are accepted as reasonable in the literature, the g values and anisotropic hyperfine couplings were calculated, taking into account only one-center integrals. The first order contributions $A_{ii}{}^1$ (Formula 4) were: $A_{xx}{}^1=48.5\times10^{-4}$, $A_{yy}{}^1=48.5\times10^{-4}$, and $A_{zz}{}^1=-97.0\times10^{-4}$ cm^{-1}. The second order contributions were calculated with approximate formulas[3]:

$$A_{xx}{}^2=P'[\Delta g_{xx}-(3/14)\Delta g_{yy}],$$
$$A_{yy}{}^2=P'[\Delta g_{yy}-(3/14)\Delta g_{xx}],$$
$$A_{zz}{}^2=P'[\Delta g_{zz}+(3/14)\Delta g_{yy}+(3/14)\Delta g_{xx}], \tag{9}$$

where $P'=g_e\beta_e g_{\text{Cu}}\beta_N\langle r_{\text{Cu}}{}^{-3}\rangle=315.98\times10^{-4}$ cm^{-1}.

These formulas yield a pseudo contact interaction of 12.9×10^{-4} cm^{-1} and anisotropic interactions: $A_{xx}{}^2=-8.8\times10^{-4}$, $A_{yy}{}^2=-6.9\times10^{-4}$, and $A_{zz}{}^2=+15.7\times10^{-4}$ cm^{-1}. Adding these values to the first order contributions, we obtained: $A_{xx}=39.7\times10^{-4}$, $A_{yy}=41.6\times10^{-4}$, and $A_{zz}=-81.3\times10^{-4}$ cm^{-1}. These values agree rather well with the observed ones, but the anisotropy in the xy plane is too small and the order of A_{xx} and A_{yy} is even reversed.

It turns out, however, that a calculation with the formula derived in this paper (Eq. 8) yields much better results, taking into account only one-center contributions. It is expected that more-center integrals may be neglected, because of the r^{-3} dependency of the

TABLE II. Experimentally determined[a] and calculated values for g_{ii}, A_{ii} [b,c] and a_{iso} [b,d] for Cu(II)(*N*,*N*-diethyldiselenocarbamate)$_2$ doped in the corresponding Ni(II) complex.

	Obs	Cu	Obs	Calc	Se$_1$	Obs	Calc	Se$_2$	Obs	Calc
g_1	2.0511±0.0001	A_{xx}	36.4±0.5	33.4	A_1	57.4±0.3	54.6	A_1	57.8±0.5	54.6
g_2	2.0021±0.0002	A_{yy}	28.8±0.5	28.5	A_2	−26.4±0.3	−26.3	A_2	−25.5±0.7	−26.4
g_3	1.9943±0.0002	A_{zz}	−65.2±0.5	−62.0	A_3	−31.0±0.6	−28.3	A_3	−32.3±1.7	−28.2
		a_{iso}	−79.3±0.3		a_{iso}	48.0±0.2		a_{iso}	45.6±0.3	

[a] See Ref. 8. Footnotes b, c, and d have the same meanings as in Table I.

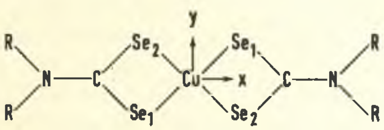
TABLE III. Observed and calculated (between parentheses) angles of principal axes relative to the axes of the A^{Cu} tensor, in degrees.

	g_1	g_2	g_3
A_{xx}^{Cu}	88.1±1.2	148.3±0.4	58.4±0.3
A_{yy}^{Cu}	2.1±1.1	88.7±1.2	91.5±0.7
A_{zz}^{Cu}	89.4±0.1	58.4±0.4	31.7±0.4
	A_1^{Se2}	A_2^{Se2}	A_3^{Se2}
A_{xx}^{Cu}	138.6±1.1(146.8)	48.8±0.9(56.8)	91.7±3.2(90.6)
A_{yy}^{Cu}	48.6±1.1(56.8)	41.6±1.1(33.2)	90.0±3.5(90.5)
A_{zz}^{Cu}	88.8±0.1(89.2)	91.1±4.7(89.9)	175.2±1.1(179.2)
	A_1^{Se1}	A_2^{Se1}	A_3^{Se1}
A_{xx}^{Cu}	38.4±0.9(33.3)	128.3±1.0(123.2)	92.6±0.6(88.3)
A_{yy}^{Cu}	51.6±0.9(56.7)	38.5±0.8(33.3)	87.9±0.9(90.6)
A_{zz}^{Cu}	89.2±0.1(91.1)	93.3±1.1(88.6)	3.4±1.0(1.8)

interactions. The resulting values are listed in Table I, after subtraction of a pseudo contact interaction of 8.2×10^{-4} cm^{-1}. Although the anisotropy in the *xy* plane is still not big enough, the order of A_{xx} and A_{yy} is right.

B. Cu(II)(*N*,*N*-Diethyldiselenocarbamate)$_2$; Cu(dsc)$_2$

After the EPR investigations on the *n*-butyl compound[7] we did also single crystal EPR measurements on the complex



R = ethyl

doped in the Ni(II) compound.[8] The central part of the latter compound is planar, and has a nearly D_{2h} symmetry.[9] The measured principal values of the *g*-tensor, and the hyperfine coupling tensors of the central copper atom and the ligand selenium atoms are listed in Table II. The principal axes of the A^{Cu} tensor coincide with the *x*, *y*, and *z* axes (the *x* and *y* axis being the bisectors of the angles Se$_1$–Cu–Se$_2$); the angles of the other principal axes relative to these are listed in Table III.

The approximate equations (9) are derived under the assumption that the principal axes of the *g* and *A* tensor coincide. Table III illustrates that this is no longer the case for the tensors in Cu(dsc)$_2$, and hence Eq. (9) cannot be applied. With Eq. (8), the anisotropic hyperfine couplings of the copper atom as well as of the selenium atoms have been calculated, again using the iterative extended Hückel method and taking into account only one center integrals. The resulting principal values are listed in Table II, the angles of the principal axes relative to those of the A^{Cu} tensor in Table III. Calculated *g* values are not listed, because they are affected very much by neighboring molecules, as will be published later. These molecules do not affect the hyperfine couplings, because of the r^{-3} dependency of these interactions. The principal values are in very good agreement with the experiment and the order of all couplings is right. The average difference between the observed and calculated directions of the principal axes is 4.9°, a very satisfactory result, keeping in mind the approximations of the extended Hückel method.

For the radial part of the atomic wavefunctions in the extended Hückel calculations, we used Slater-type orbitals from Refs. 10–12.

The required valence state ionization energies were taken from Ref. 13 or calculated from the data in Ref. 14.

The radial parts of the integrals containing the spin–orbit operator are approximated by the atomic spin–orbit coupling constants: λ(Cu 3*d*)[15] = 828 cm^{-1}; λ(Cu 4*p*)[16] = 925 cm^{-1}; λ(S 3*p*)[17] = 382 cm^{-1}; λ(C 2*p*)[17] = 28 cm^{-1}; λ(N 2*p*)[17] = 76 cm^{-1}; and λ(Se 4*p*)[18] = 1690 cm^{-1}. For calculating the expectation values of r^{-3}, use has been made of the Hartree–Fock functions published by Clementi.[19]

The calculations were performed at the University Computing Center on the IBM 360/50 computer.

ACKNOWLEDGMENTS

The present investigations have been carried out under the auspices of the Netherlands Foundation of Chemical Research (S.O.N.) and with the aid of the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

[1] A. H. Maki and B. R. McGarvey, J. Chem. Phys. **29**, 31 (1958).
[2] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, Inorg. Chem. **3**, 4580 (1964).
[3] W. Windsch and M. Welter, Z. Naturforsch **22a**, 1 (1967).

[4] C. P. Keijzers, H. J. M. de Vries, and A. van der Avoird, Inorg. Chem. (to be published).
[5] W. Low, *Paramagnetic Resonance in Solids* (Academic, New York, 1960), p. 43.
[6] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, Acta Cryst. **19**, 619 (1965).
[7] J. G. M. van Rens, C. P. Keijzers, and H. van Willigen, J. Chem. Phys. **52**, 2858 (1970).
[8] An elaborate report will be published soon.
[9] M. Bonamico and G. Dessy, J. Chem. Soc. A **1971**, 264.
[10] J. Richardson, W. Nieuwpoort, R. Powell, and W. Edgell, J. Chem. Phys. **36**, 1057 (1962).
[11] J. Richardson, R. Powell, and W. Nieuwpoort, J. Chem. Phys. **38**, 796 (1963).
[12] E. Clementi and D. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
[13] H. Basch, A. Viste, and H. B. Gray, Theoret. Chim. Acta **3**, 458 (1965).
[14] C. E. Moore, Natl. Bur. Stds. (U.S.) Circ. 467, Vol. I (1949); II (1952); and III (1958).
[15] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge, U. P., Cambridge, 1964), 2nd ed, p. 437.
[16] C. A. Bates, Proc. Phys. Soc. **79**, 69 (1962).
[17] A. Carrington and A. D. Mclachlan, *Introduction to Magnetic Resonance*, (Harper & Row, New York, 1967) 1st ed, p. 138.
[18] Calculated from Ref. 14.
[19] E. Clementi, IBM J. Res. Dev. Suppl. **9**, 2 (1965).