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Calculations of *g* Tensors and Hyperfine Splitting Tensors for Molecules in Their Triplet States

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The *g* tensors and hyperfine splitting (hfs) tensors of simple organic radicals in their triplet states have been calculated by using an all valence electron SCF MO method with a first order perturbation treatment. The molecular orbital spin density is partitioned into the σ- and π-electron spin delocalization (SD) terms and the rest terms of spin polarization (SP) which arise from the CI effect. The *g* tensors for CH_2 and several other carbenes which have triplet ground states and for formaldehyde in its $n\pi^*$ and $n\sigma^*$ excited triplet states are evaluated. The calculated α-proton hfs constants of CH_2 contributing from the π orbital well compare with the observed hfs constants of the triplet naphthalene and the doublet malonic acid radical. The anisotropic carbon-13 hfs constants of CH_2 are determined almost completely by the SD contribution and their absolute values are in good accord with those observed for CD_2. Contribution of the SP terms to the isotropic hfs constant is found to be fairly large. Prediction of the hfs constants in CF_2 and CHF is made.

Theoretical investigation and prediction of the *g* tensors and the hyperfine splitting (hfs) tensors of organic radicals give us valuable information on molecular geometry, identification of excited states, spin-orbit interactions, and so on in the radicals. Since measurements of the *g* tensors of molecules in their triplet states by means of electron paramagnetic resonance (EPR) spectroscopy were first reported,[1] rigorous theoretical prediction of the *g* tensors has rarely been found in the literature. The pioneering series of work done by McWeeny[2] are of course important and more recent efforts are made by Dalgaard and Linderberg[3] with a theory of electron propagator and by Nakatsuji and Hirao[4] with a symmetry-adapted cluster expansion. However, most of theoretical calculations carried out hitherto have been focused the zero-field splitting constants by using the π-electron approximation.

Quite recently, accurate principal *g* values have become available with the improvement of the EPR technique. For example, the observed deviation of the *g* values of triplet deutero methylene CD_2 from a free electron g_e is very large (0.0027—0.0285)[5,6] in comparison with those of organic (doublet) free radicals, for example 0.0003 in the CH_3 radical.[7] The present paper first intends to analyze the *g* tensors of CH_2 and other carbene radicals in their triplet states. The methylene radical has two unpaired electrons, one in a σ MO and the other in a π MO, so that the radical is supposed to have a dual characteristic of σ and π radicals. By partitioning an MO set, a total spin density operator is expressed as a sum of the MO spin density operators for the σ and π MO's in which an odd electron is placed and higher order terms arising from the CI effect. The former yields σ and π electron spin delocalization effect that extends over the entire system and the latter the spin polarization effect. We also report the results of our calculation on the α-proton and carbon 13 hyperfine splitting (hfs) tensors for CH_2 and the carbon 13 and fluorine 19 hfs tensors for CF_2 and CHF.

Spin Density Analysis

A method of spin density analysis which will be described below is a traditional one but we show that the method can be applied to any kinds of molecules in their triplet states, though a way of construction of MO's is restricted by the symmetry of a molecule to be considered. The spin density of paramagnetic radicals will be analyzed by a partitioning technique for the spin density operators and the spin density matrices. In this connection, we try to obtain some useful concepts and relationships which will be able to elucidate properties of the spin density. The method will explore the mechanisms of spin polarization and spin delocalization in triplet molecules.

According to McConnell,[8] a normalized spin density function $\rho(x, y, z)$ at a spatial point x, y, z whose origin is suitably taken in a molecule is defined as

$$\rho(x, y, z) = S_z^{-1}\sum_k{}' \langle \Psi, \hat{S}_{zk}\Psi \rangle_k. \qquad (1)$$

Here, Ψ is the complete wave function of a paramagnetic molecule, which is an eigenfunction of the total z component of the electron spin angular momentum operator $\hat{S}_z = \sum_k \hat{S}_{zk}$ with eigenvalue S_z, $\hat{S}_{zk}$ being the z component of spin angular momentum for electron *k*. The quantity $\langle \Psi, \hat{S}_{zk}\, \Psi \rangle_k$ denotes a matrix element to be calculated by integrating over the spin and space coordinates of all the electrons except the space coordinates of electron *k*. The prime on the summation symbol indicates that after the sum has been carried out the indices *k* should be dropped. Equation 1 shows that a quantity $\rho(x, y, z)$ gives an expectation value of $\hat{S}_z$ at point x, y, z. The circumflex symbol denotes an operator quality hereafter.

If one expands Ψ, a single determinant and/or a linear combination of them, in terms of orthonormal functions ϕ_i, one can write $\rho(x, y, z)$ in terms of the density matrix referred to these discrete bases, $\rho = [\rho_{ij}]$;

$$\rho(x, y, z) = \sum_{i,j} \rho_{ij}\phi_j^*\phi_i. \qquad (2)$$

The spin density function is associated with the one-particle density matrix $\gamma_1(x'; x)$;[2]

$$\rho(x, y, z) = S_z^{-1}\int \hat{S}_{z1}\gamma_1(x_1'; x_1)d\tau, \tag{3}$$

which shows that if the so-called natural spin-orbitals are used to constract Ψ then $\rho(x, y, z)$ is diagonalized, though we will not follow this procedure. We can define a normalized spin density operator $\hat{\rho}$ by the relation

$$\langle\phi_i, \hat{\rho}\phi_j\rangle = \rho_{ij}, \tag{4}$$

or using Dirac's bra-ket notation we write

$$\hat{\rho} = \sum_{i.j}|\phi_i\rangle\rho_{ij}\langle\phi_j| = \sum_{i.j}\hat{\rho}_{ij} = \sum_{i.j}\rho_{ij}\hat{P}_{ij}. \tag{5}$$

The last equation of Eq. 5 indicates that $\hat{\rho}$ can be expanded in terms of the projection (the transition-projection in the strict sense) operators $\hat{P}_{ij}\equiv|\phi_i\rangle\langle\phi_j|$.

When one introdues a row matrix $|\phi\rangle\equiv[|\phi_i\rangle]$, Eq. 5 is written compactly as

$$\hat{\rho} = |\phi\rangle\boldsymbol{\rho}\langle\phi|. \tag{6}$$

If molecular orbital functions are chosen as the basis $\{|\phi_i\rangle\}$, the matrix $\boldsymbol{\rho}$ may be called an MO spin density matrix and $\hat{\rho}_{ij}$ an MO spin density operator for orbitals ϕ_i and ϕ_j. The total MO spin density operator $\hat{\rho}$ is of course self-adjoint and normalized to unity; $\mathrm{tr}(\hat{\rho})=\sum_i\rho_{ij}=1$.

If one employs another set of $|\chi\rangle$ whose elements $|\chi_\mu\rangle$ are linearly independent but not necessarily orthonormal, first one constructs a set of orthonormalized vectors $|e\rangle=|\chi\rangle\boldsymbol{S}^{-1/2}$ with $\boldsymbol{S}\equiv\langle\chi|\chi\rangle$ (Löwdin's symmetric orthonormalization[9]), then one obtains instead of Eqs. 5 and 6

$$\hat{\rho} = \sum_{\mu,\nu}|e_\mu\rangle\bar{\rho}'_{\mu\nu}\langle e_\nu| = \sum_{\mu,\nu}\hat{\bar{\rho}}'_\nu = e\rangle\bar{\boldsymbol{\rho}}'\langle e|. \tag{7}$$

Further if one puts $\boldsymbol{S}^{-1/2}\bar{\rho}'\boldsymbol{S}^{-1/2}\equiv\bar{\boldsymbol{\rho}}$, then one has

$$\hat{\rho} = |\chi\rangle\boldsymbol{S}^{-1/2}\bar{\boldsymbol{\rho}}'\boldsymbol{S}^{-1/2}\langle\chi| = \sum_{\mu,\nu}\bar{\boldsymbol{\rho}}_{\mu\nu} = |\chi\rangle\bar{\boldsymbol{\rho}}\langle\chi|. \tag{8}$$

The relationship $\bar{\rho}'=\boldsymbol{S}^{1/2}\bar{\rho}\boldsymbol{S}^{1/2}$ is important because it is useful in a general case which contains the overlap effect discussed by McConnell.[10] When $|\chi\rangle$ is chosen as a set of AO's, $\bar{\boldsymbol{\rho}}$ may be called the AO spin density matrix and $\hat{\bar{\rho}}_{\mu\nu}$ the AO spin density operator for AO's $|\chi_\mu\rangle$ and $|\chi_\nu\rangle$. Note that $\mathrm{tr}(\hat{\bar{\rho}})=\mathrm{tr}(\bar{\rho}')=\mathrm{tr}(\boldsymbol{S}^{-1/2}\bar{\boldsymbol{\rho}}\boldsymbol{S}^{-1/2})=\mathrm{tr}(\bar{\boldsymbol{\rho}}\boldsymbol{S})=1$. When $|\phi_i\rangle$ is expressed as a linear combination of $|\chi_\mu\rangle$'s

$$|\phi_i\rangle = |\chi\rangle\boldsymbol{C}_i \text{ or } |\phi\rangle = |\chi\rangle\boldsymbol{C}, \tag{9}$$

the matrices $\bar{\boldsymbol{\rho}}$ and $\boldsymbol{\rho}$ are related to one another in the way as[8]

$$\bar{\boldsymbol{\rho}} = \langle\eta|\hat{\rho}|\eta\rangle = \langle\eta|\phi\rangle\boldsymbol{\rho}\langle\phi|\eta\rangle = \boldsymbol{C}\boldsymbol{\rho}\boldsymbol{C}^\dagger, \tag{10}$$

where $|\eta\rangle=|\chi\rangle\boldsymbol{S}^{-1}$, that is $|\eta\rangle$ is the reciprocal vector with respect to $|\chi\rangle$. Note that Eq. 10 is valid in either case that $|\chi\rangle$ is orthonormal or not.

Now we mention the essence of the present method. First, we partition an MO set $|\phi\rangle$ into appropriate subsets, σ and π MO's *etc.*, and AO's $|\chi\rangle$ into those centered at atom A, B, $\cdots$:

$$\begin{aligned}|\phi\rangle &\equiv (|\phi_\sigma\rangle|\phi_\pi\rangle\cdots),\ |\phi_\sigma\rangle \equiv (|\phi_{\sigma1}\rangle|\phi_{\sigma2}\rangle\cdots),\\ |\chi\rangle &\equiv (|\chi_A\rangle|\chi_B\rangle\cdots),\ |\chi_A\rangle \equiv (|\chi_{A1}\rangle|\chi_{A2}\rangle\cdots).\end{aligned} \tag{11}$$

Since the total MO spin density operator $\hat{\rho}$ may be considered to be totally symmetric only if those partitioned $|\phi_\sigma\rangle$ and $|\phi_\pi\rangle$ belong to irreducible representations of the σ and π symmetries (this is the case for Hartree-Fock MO's), the relationships $\langle\phi_\sigma|\hat{\rho}|\phi_\pi\rangle=0$ *etc.* hold and we obtain

$$\begin{aligned}\hat{\rho} &= \hat{\rho}_{\sigma\sigma} + \hat{\rho}_{\pi\pi} + \cdots\\ &= |\phi_\sigma\rangle\boldsymbol{\rho}_{\sigma\sigma}\langle\phi_\sigma| + |\phi_\pi\rangle\boldsymbol{\rho}_{\pi\pi}\langle\phi_\pi| + \cdots.\end{aligned} \tag{12}$$

Here, the whole MO spin density matrix $\boldsymbol{\rho}$ is in general diagonalized in such a way that

$$\boldsymbol{\rho} = \begin{array}{c|c:c:c|} & \sigma_1\sigma_1\cdots & \pi_1\pi_2\cdots & \\ \begin{array}{c}\sigma_1\\ \sigma_2\\ \vdots\end{array} & \boldsymbol{\rho}_{\sigma\sigma} & 0 & \\ \hdashline \begin{array}{c}\pi_1\\ \pi_2\end{array} & 0 & \boldsymbol{\rho}_{\pi\pi} & \\ \hdashline & & & \end{array}. \tag{13}$$

In short, the corresponding MO spin density operators $\hat{\rho}_{\sigma\sigma}$ and $\hat{\rho}_{\pi\pi}$ yield leading terms of the spin density for σ-type and π-type radicals, respectively. These terms actually manifest the so-called spin-delocalization (SD) effect.[11] The remaining higher order terms which are not shown in Eq. 12 come from the CI effect and contribute to spin-polarization.[11] Therefore, total $\hat{\rho}$ is a sum of operators which count out the spin density due to spin-delocalization and that which yields spin-polarization:

$$\hat{\rho} = \hat{\rho}^{\mathrm{SD}} + \hat{\rho}^{\mathrm{SP}}, \tag{14}$$

where one should note that $\mathrm{tr}(\hat{\rho}^{\mathrm{SD}})=1$ and $\mathrm{tr}(\hat{\rho}^{\mathrm{SP}})=0$.

What follows is an extention of the spin density formulation. Though we do not actually apply it to the present numerical analyses, it will be useful for more detailed exploration of the mechanism of spin polarization and spin delocalization. The degree of localization of the spin density of atom A is measured by

$$\bar{\rho}_A = \sum_{\mu\in A}\langle\eta_\mu|\hat{\rho}|\eta_\mu\rangle = \bar{\rho}_A{}^{\mathrm{SD}} + \bar{\rho}_A{}^{\mathrm{SP}}, \tag{15}$$

where

$$\bar{\rho}_A{}^{\mathrm{SD}} = \sum_{\mu\in A}\langle\eta_\mu|\hat{\rho}^{\mathrm{SD}}|\eta_\mu\rangle \tag{16}$$

and

$$\bar{\rho}_A{}^{\mathrm{SP}} = \sum_{\mu\in A}\langle\eta_\mu|\hat{\rho}^{\mathrm{SP}}|\eta_\mu\rangle. \tag{17}$$

Then, one can say that the complete delocalization takes place on atom A when $\bar{\rho}_A=0$, and the complete localization occurs on atom A when $\bar{\rho}_A=1$. In the case that atom A is considered to be a radical center, the measure of delocalization of the spin density on the radical center is expressed as $1-\bar{\rho}_A$. On the other hand, a measure of localization of the spin density in bond A–B is given by

$$\bar{\rho}^{AB} = \sum_{\mu\in A,\ \nu\in B}\langle\eta_\mu|\hat{\rho}|\eta_\nu\rangle, \tag{18}$$

which cannot be assigned to either of atom A and atom B.

Since the Hermitian matrix $\boldsymbol{\rho}_{\sigma\sigma}$ can be diagonalized such that $\boldsymbol{d}_\sigma=\boldsymbol{U}_\sigma{}^\dagger\boldsymbol{\rho}_{\sigma\sigma}\boldsymbol{U}_\sigma$ ($\boldsymbol{U}_\sigma$ is a unitary matrix), one obtains

$$\hat{\rho}_{\sigma\sigma} = |\phi_\sigma'\rangle\boldsymbol{d}_\sigma\langle\phi_\sigma'|, \tag{19}$$

with

$$|\phi_\sigma'\rangle = |\phi_\sigma\rangle\boldsymbol{U}_\sigma. \tag{20}$$

We may call $\boldsymbol{d}_\sigma$ an MO occupation spin density and $|\phi_\sigma'\rangle$ a spin density naturalized MO. A similar definition can be made for π MO's and higher symmetry MO's.

Using a unitary matrix $\boldsymbol{U}$ which diagonalizes $\boldsymbol{\rho}$, one can obtain a relationship which is similar to Eq. 10:

$$\vec{\boldsymbol{d}} = \boldsymbol{C}'\boldsymbol{d}\boldsymbol{C}'^{\dagger},\ \text{with}\ \boldsymbol{C}' = \boldsymbol{U}^{\dagger}\boldsymbol{C}\boldsymbol{U}. \tag{21}$$

The quantity d^{A} defined by

$$d^{\mathrm{A}} = \sum_{\mu\in\mathrm{A}} d_{\mu\mu} = \sum_{\mu\in\mathrm{A}} \langle \eta_{\mu}'|\hat{\rho}|\eta_{\mu}'\rangle \tag{22}$$

may be called an atomic occupation spin density on atom A, while $d_{\mu\mu}$ may be termed as an AO occupation spin density centered at atom A.

g Tensors of Triplet Molecules

First we describe the method of calculation of the 3×3 matrix elements $g^{ij}(i,j=\mathrm{x, y, z})$ of the g tensor. It is well known that in a π doublet radical certain negative spin density occurs on the proton in the molecular plane through the σ-π interaction.[8] This also will be the case for triplet radicals. Assuming such perturbation is small, we may construct a total wavefunction so as to mix the ground state function with excited functions by making use of a first-order perturbation theory.

Let $\Psi^{\mathrm{M}}_{\mathrm{G}}(\mathrm{M}=-1,\ 0,\ 1)$ be the Slater determinant of the triplet ground state of a molecule, in which non-degenerate molecular orbitals ϕ_{m} and ϕ_{n} accomodate one unpaired electron each:

$$\Psi^{\mathrm{M}}_{\mathrm{G}} = |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m\phi_n|. \tag{23}$$

The one-electron excited state determinantal wave functions which are eigenfunctions of $\hat{S}_{\mathrm{z}}$ and $\hat{S}^2$ are divided into the following four classes:

$$\left.\begin{aligned} \Psi^{\mathrm{M}}_{i\to m} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_m \cdots \phi_m\phi_n|, \\ \Psi^{\mathrm{M}}_{m\to k} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_k\phi_n|, \end{aligned}\right\} \tag{24}$$

$$\left.\begin{aligned} \Psi^{\mathrm{M}}_{i\to k}(\mathrm{A}) &= (\Psi_1{}^{(\mathrm{m})}+\Psi_2{}^{(\mathrm{m})})/\sqrt{2}, \\ \Psi^{\mathrm{M}}_{i\to k}(\mathrm{B}) &= (\Psi_1{}^{(\mathrm{m})}-\Psi_2{}^{(\mathrm{m})}-2\Psi_3{}^{(\mathrm{m})})/\sqrt{6}, \\ \text{and/or}\quad \Psi^{\mathrm{M}}_{i\to k}(\mathrm{C}) &= (\Psi_1{}^{(\mathrm{m})}-\Psi_2{}^{(\mathrm{m})}-2\Psi_3{}^{(n)})/\sqrt{6} \end{aligned}\right\} \tag{25}$$

with

$$\left.\begin{aligned} \Psi_1{}^{(\mathrm{m})} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_k \cdots \phi_m\phi_n|, \\ \Psi_2{}^{(\mathrm{m})} &= |\phi_1\bar{\phi}_1 \cdots \phi_k\bar{\phi}_i \cdots \phi_m\phi_n|, \\ \Psi_3{}^{(\mathrm{m})} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\phi_k \cdots \bar{\phi}_m\phi_n|, \\ \Psi_3{}^{(\mathrm{n})} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\phi_k \cdots \phi_m\bar{\phi}_n|, \end{aligned}\right\} \tag{26}$$

where the suffices i and k refer to doubly occupied MO's and vacant MO's in $\Psi^{\mathrm{M}}_{\mathrm{G}}$, respectively. By direct calculation, we found that the former two (Eq. 24) contribute to the g tensor ffnd the latter two (Eq. 25) have an effect to the σ-π interaction in hfs tensor.

After mixing the former two functions, $\Psi^{\mathrm{M}}_{i\to m}$ and $\Psi^{\mathrm{M}}_{m\to k}$, with $\Psi^{\mathrm{M}}_{\mathrm{G}}$ through the spin-orbit interaction $\hat{H}_{\mathrm{LS}}=\sum_{t,j}\zeta_t\hat{L}_{jt}\cdot\hat{S}_j$ where $\hat{L}_{jt}$ is the orbital angular momentum operator for the jth electron with respect to the tth nucleus and ζ_t is the spin-orbit coupling constant, the total wave function $\Psi^{\mathrm{M}}_{\mathrm{T}}$ to be used for the calculation of the g tensor is expressed as

$$\Psi^{\mathrm{M}}_{\mathrm{T}} = \Psi^{\mathrm{M}}_{\mathrm{G}} - \sum_{\mathrm{I,M'}} \lambda^{\mathrm{M'}}_{\mathrm{I}}\Psi^{\mathrm{M'}}_{\mathrm{I}}, \quad (\mathrm{M'}=-1,\ 0,\ 1) \tag{27}$$

where

$$\lambda^{\mathrm{M'}}_{\mathrm{I}} = \langle \Psi^{\mathrm{M'}}_{\mathrm{I}}|\hat{H}_{\mathrm{LS}}|\Psi^{\mathrm{M}}_{\mathrm{G}}\rangle/[E(\Psi^{\mathrm{M'}}_{\mathrm{I}})-E(\Psi^{\mathrm{M}}_{\mathrm{G}})], \tag{28}$$

and I refers to $i\to m$ and $m\to k$.

As is well known, the anisotropic g tensor in the expression of the effective spin Hamiltonian $\hat{H}_{\mathrm{eff}}=\mu_{\mathrm{B}}H\cdot g\cdot\hat{S}'$, where μ_{B} is the electronic Bohr magneton, H the external magnetic field, and $\hat{S}'$ the ficititious spin, is estimated by the aid of the true Hamiltonian for the magnetic interaction $\hat{H}=\mu_{\mathrm{B}}H\cdot(\hat{L}+g_{\mathrm{e}}\hat{S})$, g_{e} being the gyromagnetic factor for a free electron ($g_{\mathrm{e}}=2.00232$). That is, after calculating the 3×3 matrices for $\hat{H}_{\mathrm{eff}}$ and $\hat{H}$ by using $\Psi^{\mathrm{M}}_{\mathrm{T}}(\mathrm{M}=-1,\ 0,\ 1)$ as bases, and comparing the corresponding matrix elements term by term, one obtains the components of the g tensors as in the following:

$$g^{\mathrm{xy}} = g_{\mathrm{e}}\delta_{\mathrm{xy}} + \Delta g^{\mathrm{xy}}, \tag{29}$$

$$\Delta g^{\mathrm{xy}} = \Delta g^{\mathrm{xy}}_{m} + \Delta g^{\mathrm{xy}}_{n}, \tag{30}$$

$$\Delta g^{\mathrm{xy}}_{m} = \sum_{i}\Delta g^{\mathrm{xy}}_{mi} - \sum_{k}\Delta g^{\mathrm{xy}}_{mk}, \tag{31}$$

$$\Delta g^{\mathrm{xy}}_{mi} = (2S)^{-1}(\Lambda^{\mathrm{xy}}_{mi}+\Gamma^{\mathrm{xy}}_{mi})/[E(\Psi^{\mathrm{M'}}_{i\to m})-E(\Psi^{\mathrm{M}}_{\mathrm{G}})], \tag{32}$$

$$\Lambda^{\mathrm{xy}}_{mi} = \langle\phi_m|\sum_{t,j}\hat{L}^{\mathrm{x}}_{jt}|\phi_i\rangle\langle\phi_i|\sum_{t,j}\zeta_t\hat{L}^{\mathrm{y}}_{jt}|\phi_m\rangle, \tag{33}$$

$$\Gamma^{\mathrm{xy}}_{mi} = \langle\phi_m|\sum_{t,j}\hat{L}^{\mathrm{y}}_{jt}|\phi_i\rangle\langle\phi_i|\sum_{t,j}\zeta_t\hat{L}^{\mathrm{x}}_{jt}|\phi_m\rangle, \tag{34}$$

and so on. If the molecular axes coincide with principal axes of the g tensor, the two terms in the numerator of Eq. 32 reduce to one term. We can thus calculate the principal values of g by diagonalizing the matrix Δg^{xy} or g^{xy}.

Hyperfine Splitting Tensors

For triplet radicals having the ground state wave function $\Psi^{\mathrm{M}}_{\mathrm{G}}$ of Eq. 23, the leading term of the total MO spin density operator $\hat{\rho}$, as given in Eq. 12, becomes

$$\hat{\rho}(\Psi^{\mathrm{M}}_{\mathrm{G}};\Psi^{\mathrm{M}}_{\mathrm{G}}) = \hat{\rho}^{\mathrm{SD}}_{\mathrm{mm}} + \hat{\rho}^{\mathrm{SD}}_{\mathrm{nn}}, \tag{35}$$

that is, corresponding to Eq. 13,

$$\rho(\Psi^{\mathrm{M}}_{\mathrm{G}};\Psi^{\mathrm{M}}_{\mathrm{G}}) = \begin{array}{c} \\ \\ m \\ n \\ \\ \end{array}\!\!\begin{array}{cccc} & m & n & \\ \hline 0 & \vdots & \vdots & \\ \cdots\cdots & 0.5 & \vdots & 0 \\ \cdots\cdots & \cdots & 0.5 & \\ & 0 & & 0 \end{array}. \tag{36}$$

In the SCF framework, $\Psi^{\mathrm{M}}_{\mathrm{G}}$ does not mix with $\Psi^{\mathrm{M}}_{i\to m}$ and $\Psi^{\mathrm{M}}_{m\to k}$ of Eq. 24 due to the Brillouin theorem. Also, $\hat{\rho}(\Psi^{\mathrm{M}}_{\mathrm{G}};\Psi^{\mathrm{M}}_{i\to k}(\mathrm{A}))=1/\sqrt{2}(-\hat{P}_{ik}+\hat{P}_{ik})=0$. Therefore, the ground state wave function $\Psi^{\mathrm{M}}_{\mathrm{T}}$ can be improved by the mixing of only $\Psi^{\mathrm{M}}_{i\to k}(\mathrm{B})$ and $\Psi^{\mathrm{M}}_{i\to k}(\mathrm{C})$ of Eq. 25:

$$\Psi^{\mathrm{M}}_{\mathrm{T}} = \Psi^{\mathrm{M}}_{\mathrm{G}} + \sum_{i,k}\{\lambda^{(\mathrm{m})}_{ik}\Psi^{\mathrm{M}}_{i\to k}(\mathrm{B})+\lambda^{(\mathrm{n})}_{ik}\Psi^{\mathrm{M}}_{i\to k}(\mathrm{C})\}, \tag{37}$$

where

$$\left.\begin{aligned} \lambda^{(\mathrm{m})}_{ik} &= \frac{1}{\sqrt{6}}[3(mi|km)+(ni|kn)]/\Delta E^{(\mathrm{m})}, \\ \lambda^{(\mathrm{n})}_{ik} &= \frac{1}{\sqrt{6}}[3(ni|kn)+(mi|km)]/\Delta E^{(\mathrm{n})}, \end{aligned}\right\} \tag{38}$$

$$\left.\begin{aligned} \Delta E^{(\mathrm{m})} &= E(\Psi^{\mathrm{M}}_{i\to k}(\mathrm{B})) - E(\Psi^{\mathrm{M}}_{\mathrm{G}}), \\ \Delta E^{(\mathrm{n})} &= E(\Psi^{\mathrm{M}}_{i\to k}(\mathrm{C})) - E(\Psi^{\mathrm{M}}_{\mathrm{G}}), \end{aligned}\right\} \tag{39}$$

and

$$(pq|rs) = \iint \phi^{*}_{p}(1)\phi_{\mathrm{q}}(1)(e^2/r_{12})\phi^{*}_{r}(2)\phi_{s}(2)\mathrm{d}v(1)\mathrm{d}v(2). \tag{40}$$

We thus finally obtain the total MO spin density

$$\rho(\Psi^{\mathrm{M}}_{\mathrm{T}};\Psi^{\mathrm{M}}_{\mathrm{T}}) = \rho^{\mathrm{SD}}_{mm} + \rho^{\mathrm{SD}}_{nn} + \rho^{\mathrm{SP}}, \tag{41}$$

$$\rho^{\mathrm{SP}} = \rho_{ik}^{(\mathrm{m})} + \rho_{ik}^{(\mathrm{n})} = -\frac{1}{\sqrt{6}}(\lambda_{ik}^{(\mathrm{m})} + \lambda_{ik}^{(\mathrm{n})}). \tag{42}$$

The AO spin density contribution due to spin polarization is obtained by means of Eq. 10:

$$(\bar{\rho}^{\mathrm{SP}})_{\mu\nu} = \sum_i\sum_k(\rho^{\mathrm{SP}})_{ik}(C_{\mu i}C_{\nu k}^* + C_{\mu k}C_{\nu i}^*). \tag{43}$$

The MO and AO spin density matrices necessary for the present calculation are listed in Appendix A.

The matrix elements of the anisotropic hfs tensor for nucleus N, $A^{\mathrm{N}ij}$, are calculated by[12)]

$$A^{\mathrm{N}ij} = tr(\rho\Omega^{\mathrm{N}ij}), \quad (i, j=\mathrm{x, y, z}) \tag{44}$$

$$\Omega_{rs}^{\mathrm{N}ij} = -g\mu_{\mathrm{B}}\hbar\gamma_{\mathrm{N}}t_{ij}(\chi_r\chi_s), \tag{45}$$

$$t_{ij}(\chi_r\chi_s) = \langle\chi_r(1)|r_{1\mathrm{N}}^{-5}(r_{1\mathrm{N}}^2\delta_{ij} - 3r_{1\mathrm{N}}^i r_{1\mathrm{N}}^j)|\chi_s(1)\rangle. \tag{46}$$

Here, $t_{ij}(\chi_r\chi_s)$ is the electron-nuclear dipolar interaction integral and γ_{N} the gyromagnetic ratio of nucleus N. By diagonalizing the matrix $A^{\mathrm{N}ij}$, we obtain the principal values of the anisotropic hfs tensor and the direction cosines between the molecular and principal axes. The dipolar integrals $t_{ij}(\chi_r\chi_s)$ are evaluated by using the following approximations: (1) All the three-center integrals and all the two-center integrals involving the product $\chi_r\chi_s$ in which χ_r and χ_s belong to different atoms are neglected and the remaining one- and two-center integrals are analytically evaluated over the Slater-type orbitals; (2) the one-center dipolar integrals are improved by the use of Löwdin's SCF AO's.[13)] Analytical formulas of the dipolar integrals are given in Appendix B.

The isotropic hfs constant for nucleus N is given by[12)]

$$a^{\mathrm{N}} = tr(\rho\mathrm{Q})^{\mathrm{N}}, \tag{47}$$

$$(\mathrm{Q}^{\mathrm{N}})_{rs} = (8\pi/3)g\mu_{\mathrm{B}}\hbar\gamma_{\mathrm{N}}\langle\chi_r(1)|\delta(r_{1\mathrm{N}})|\chi_s(1)\rangle, \tag{48}$$

δ being the Dirac δ-function. The one-center integrals $<\chi_r(1)|\delta(\mathrm{r}_{1\mathrm{N}})|\chi_s(1)>$ are evaluated over the Löwdin SCF AO's.[13)]

Results and Discussion

First, we apply the above-mentioned calculation schemes to the g tensor of the methylene radical in its triplet state $^3\mathrm{B}(\mathrm{n}, \pi)$. The molecular geometry is as follows;[14)] the C–H bond length 1.078 Å, the HCH bond angle 136°. The electron configuration is $(1\mathrm{a}_1)^2(1\mathrm{b}_1)^2(2\mathrm{a}_1)^1(1\mathrm{b}_2)^1(3\mathrm{a}_1)^0(2\mathrm{b}_1)^0$, the six valence electrons being taken into account. The molecular z axis is taken in the molecular plane so as to bisect the HCH angle and the y axis perpendicular to the molecular plane. The MO wave functions are obtained by using Roothaan's open-shell SCF operator[15)] with the INDO approximation for integrals over AO's.[16)] A pseudopotential is added to Roothaan's operator in order to obtain fast and perfect convergence.[17)] The exchange energy between the first excited singlet and the ground triplet states, $2K_{mn}$, is calculated to be 1.74 eV which is much larger than the electronic Zeeman energy. This gives convincing proofs of our assumption that the g tensor can be calculated by a perturbation treatment.

Methylene has the characteristics of both the double σ radical and the doublet π radical, since one of the two unpaired electrons occupy the σ orbital $2\mathrm{a}_1$ and the other the π orbital $1\mathrm{b}_2$. This situation is well expressed by Eq. 30 which can be written in this case as

$$\Delta g^{xy} = \Delta g^{xy}(2\mathrm{a}_1) + \Delta g^{xy}(1\mathrm{b}_2). \tag{49}$$

With Eqs. 30—34 and their analogues, the contribution of the one-electron excited wave functions of the type shown in Eq. 24 to the diagonal elements of Δg is calculated to be as in the following: (0, 12, 0) for $1\mathrm{b}_1 \rightarrow 2\mathrm{a}_1$, (0, −12, 0) for $2\mathrm{a}_1 \rightarrow 2\mathrm{b}_1$, (0, 0, 15) for $1\mathrm{b}_1 \rightarrow 1\mathrm{b}_2$, (−10, 0, 0) for $1\mathrm{b}_2 \rightarrow 3\mathrm{a}_1$, and (0, 0, −19) for $1\mathrm{b}_2 \rightarrow 2\mathrm{b}_1$, where the figures in parentheses denote the value of $(\Delta g^{xx}, \Delta g^{yy}, \Delta g^{zz}) \equiv \Delta g$ in units of 10^{-5}. The Δg values which come from other wave functions, $1\mathrm{a}_1 \rightarrow 2\mathrm{a}_1$, $1\mathrm{a}_1 \rightarrow 1\mathrm{b}_2$, and $2\mathrm{a}_1 \rightarrow 3\mathrm{a}_1$, are found to be very close to zero.

The principal values of the g tensor of methylene are then calculated to be (2.00222, 2.00232, 2.00228) which lie close to the free electron value g_{e}. We have confirmed that the structural dependence is rather small; *e.g.*, $\Delta g = (-12, 2, -4)$ when ∠HCH=111° and (−8, −3, −5) when ∠HCH=150°, all in units of 10^{-5}. The observed principal values of the g tensor for CD_2 in the xenon matrix at 4K are (1.9995, 1.9984, 1.9984),[5)] which are 0.003—0.004 below our predicted values for an isolated CH_2. More recently, there have been reported much smaller g values; (1.9738, 1.9953, 1.9946) for CD_2 and (1.9742, 1.9955, 1.9942) for $^{13}\mathrm{CD}_2$ both in xenon matrices.[18)] These are not to be compared with our calculated values, since a solid solution matrix usually causes a large deviation from the g_{e} value due to intermolecular interactions with a host molecule and the effects of deuteration and molecular orientation.[19)] The tendency that the deviation from g_{e} (and also anisotropy among the principal g values) is very small in the present prediction is in accord with experimental findings for organic doublet free radicals containing carbon and hydrogen only; 0.0003 for CH_3,[20)] 0.0001 for $\mathrm{CH{=}CH_2}$,[20)] 0.0003 for $\mathrm{C{\equiv}CH}$,[21)] in their doublet ground states in solid solution matrices.

Table 1. Calculated principal g tensors of triplet molecules

	g^{xx}	g^{yy}	g^{zz}	g_{av}*)
CH_2	2.00222	2.00232	2.00228	2.00228
CF_2	2.00219	2.00348	2.00327	2.00298
$\mathrm{C(CN)}_2$	2.00228	2.00233	2.00231	2.00231
CHF	2.00291	2.00210	2.00290	2.00264
$\mathrm{H}_2\mathrm{CO}$				
$^3\mathrm{A}_2(\mathrm{n}\pi^*)$	2.00286	2.00450	2.00685	2.00474
$^3\mathrm{B}_1(\mathrm{n}\sigma^*)$	2.00244	2.00425	2.00556	2.00408

*) $g_{\mathrm{av}} = (1/3)(g^{xx} + g^{yy} + g^{zz})$

Table 1 lists the calculated principal values of the g tensor for other triplet molecules for which the very same calculation scheme has been used. Contrary to CH_2 in which the carbon atom mainly contributes to Δg because the spin-orbit interaction constant of hydrogen is negligibly small, anisotropy in CF_2 is rather large; our estimate made by the use of the partitioning method, $\Delta g = \Delta g_{\mathrm{C}} + \Delta g_{\mathrm{F}} + \Delta g_{\mathrm{F}}'$ (geometry: r(C–F)=1.3 Å, ∠FCF′=125°), is $\Delta g_{\mathrm{C}} = (-33, -1, -14)$ and $\Delta g_{\mathrm{F}} = \Delta g_{\mathrm{F}}' = (10, 58, 55)$ in units of 10^{-5}. The deviation of the simple average value of g, $g_{av}=(1/3)(g^{xx}+g^{yy}+g^{zz})$, from the g_e value is larger in CF_2 and also in CHCHO.

At the bottom of Table 1, are shown the principal values of the g tensor calculated for the excited triplet states $^3A_2(n, \pi^*)$ and $^3B_1(n, \sigma^*)$ of formaldehyde. The molecular geometry corresponding to the minimum total energy is $r(C{=}O)=1.30$ Å, $r(C{-}H)=1.10$ Å, and $\angle HCH=121°$, the z axis being taken along the C=O bond and the y axis perpendicular to the molecular plane. We have assumed a planar structure for these excited triplet states of formaldehyde, though at least the $^3A_2(n\pi^*)$ state is known to have a bent structure (out of plane angle 35°).[23)] This is simply because there are no experimental data available for the g tensors of these states and we try to compare the calculated results with the only available datum for the planar triplet benzophenone molecule.[22)] The observed g tensor of the triplet benzophenone molecule is (1.9990, 1.9994, 2.0097),[22)] the x and y axes here making angles of 60° and 30° respectively with the plane of the carbonyl group. Apart from these inclination of the x and y axes, the g^{xx} and g^{yy} values calculated for formaldehyde are larger than those observed for benzophenone, so is the case of the triplet ground state of methylene. On the contrary, the calculated g^{zz} value of formaldehyde is smaller than the experimental g^{zz} value of benzophenone, this being reversed in the case of methylene. Further investigation is needed as for whether these discrepancies are physically significant. From the experimental point of view, the two triplet excited states of formaldehyde are expected to be identified by an accurate measurement of the g tensor.

TABLE 2. MOLECULAR ORBITAL SPIN DENSITY $\rho = \rho^{SD} + \rho^{SP}$ OF CH_2

MO	$1a_1$	$1b_1$	$2a_1$	$1b_2$	$3a_1$	$2b_1$
$1a_1$	0	0	0	0	−0.032	0.0
$1b_1$	0	0	0	0	0.0	−0.018
$2a_1$	0	0	0.500	0	0	0
$1b_2$	0	0	0	0.500	0	0
$3a_1$	−0.032	0.0	0	0	0	0
$2b_1$	0.0	−0.018	0	0	0	0

The effect of spin polarization in the MO spin density ρ of CH_2 calculated by using Eq. 42 is shown in Table 2. We should note that the non-vanishing off-diagonal elements are all negative and their values are within 6.4% of the diagonal element 0.5. Table 3 lists the AO spin density $\bar{\rho}=\bar{\rho}^{SP}+\bar{\rho}^{SP}$ of CH_2. The diagonal elements for the s orbitals are proportional to the corresponding isotropic hfs constants. The AO spin density of the carbon $2p_z$ orbital is 0.5 and the sum of the remaining diagonals is 0.5. Note that the negative spin density appears on the two protons.

Table 4 shows the results on the analysis of the α-proton isotropic hfs constant, a^H, and the principal values of the α-proton anisotropic hfs tensor, A^H_{ii}(i= x, y, z), of the triplet CH_2 radical. Comparison of the third, fourth, fifth, and sixth columns shows that the anisotropic terms are determined almost completely by the spin delocalization contribution. Figures listed in the seventh column are the values per unit spin which come from the $1b_2$ π MO only, a simple double of a sum of the values in the fourth and the sixth columns since the spin density in the $1b_2$ π MO is 0.5. These values are well compared with the observed α-proton hfs constants per unit spin for triplet naphthalene[24)] and the doublet malonic acid radical.[25)] Going into details, the calculated isotropic constant is rather small; this is probably because the present perturbation treatment underestimates the contribution of spin polarization. Incidentally, a semi-quantitative estimate on a CH fragment ($S=1/2$) made by McConnell and Strathdee[26)] is as follows: $a^H=-63$, $A^H_{xx}=-40$, $A^H_{yy}=42$, $A^H_{zz}=-6$ (all in MHz), the x axis being along the $2p\pi$ carbon

TABLE 3. ATOMIC ORBITAL SPIN DENSITY $\bar{\rho}=\bar{\rho}^{SD}+\bar{\rho}^{SP}$ OF CH_2[a)]

	2s(C)	$2p_x$(C)	$2p_y$(C)	$2p_z$(C)	1s(H)	1s(H′)
2s(C)	0.114					
$2p_x$(C)	0	0.018				
$2p_y$(C)	0.171	0	0.384			
$2p_z$(C)	0	0	0	0.500		
1s(H)	−0.043	0.001	−0.080	0	−0.008	
1s(H′)	−0.043	−0.001	−0.080	0	0.010	−0.008

a) The z axis bisects the HCH angle in the molecular plane and the y axis is perpendicular to the plane.

TABLE 4. ANALYSIS OF α-PROTON hfs CONSTANTS OF TRIPLET CH_2(in MHz)

Term	Calculated contribution of spin densities						Observed	
	Total ρ	ρ^{SD}_m $(2a_1, \sigma)$	ρ^{SD}_n $(1b_2, \rho)$	ρ^{SP}_m $(2a_1, \sigma)$	ρ^{SP}_n $(1b_2, \pi)$	Contribution from π orbital only per unit spin[a)]	Naphthalene ($S=1$) per unit spin Ref. 23	Malonic acid ($S=1/2$) per unit spin Ref. 24
a^H	−12	22	0	−14	−20	−40	−67	−60
A^H_{xx}	−27	−5	−20	−1	−1	−42	−31	−31
A^H_{yy}	47	20	23	2	2	50	36	31
A^H_{zz}	−21	−16	−3	−1	−1	−8	−5	−1

a) $2(\rho^{SD}_n+\rho^{SP}_n)$

Table 5. Analysis of ^{13}C hfs constants of triplet CH_2(in MHz)

Term	Calculated contribution of spin densities							Observed		
								Wasserman *et al.*	Bernheim *et al.*	
	Total ρ	ρ^{SD}	ρ^{SD}(H)	ρ_m^{SD} $(2a_1, \sigma)$	ρ_n^{SD} $(1b_2, \pi)$	ρ_m^{SP} $(2a_1, \sigma)$	ρ_n^{SP} $(1b_2, \pi)$	Ref. 5	Ref. 18	Ref. 6
a^C	+356	+281	—	+281	0	+26	+49	247	249	245
A^C_{xx}	−76	−78	+0.3	−33	−45	+1	+1	70	53	63
A^C_{yy}	+22	+22	−0.1	+67	−45	0	0	34	31	34
A^C_{zz}	+53	+55	−0.2	−34	+89	−1	−1	35	25	30

Table 6. Prediction of the hyperfine splitting tensors of CF_2 and CHF (in MHz)

Term	CF_2						CHF								
	^{13}C			^{19}F			^{13}C			^{19}F			^{1}H		
	Total ρ	ρ^{SD}	ρ^{SP}	Total ρ	ρ^{SD}	ρ^{SP}	Total ρ	ρ^{SD}	ρ^{SP}	Total ρ	ρ^{SD}	ρ^{SP}	Total ρ	ρ^{SD}	ρ^{SP}
a	624	633	−9	113	105	8	475	462	13	84	49	35	60	66	−6
A_{xx}	−52	−51	−1	−146	−115	−31	−60	−61	1	−141	−109	−32	−23	−23	0
A_{yy}	−6	−7	1	136	106	30	4	4	0	92	70	22	37	36	1
A_{zz}	58	58	~0	10	9	1	56	57	−1	50	39	11	−14	−14	0

orbitals and the z axis along the C–H bond.

The calculated carbon 13 hfs constants of CH_2 are listed in Table 5 together with the observed values for CD_2. Comparison of the second and the third columns shows that the anisotropic terms are determined almost completely by the spin delocalization contribution as in the case of the α-proton hfs constants, while the isotropic term receives a considerable effect of spin polarization. The fourth column shows the delocalization contribution from the spin densities on the hydrogen atoms to hfs constants; the effect of hydrogen is negligibly small. In the fifth and the sixth columns is divided the total contribution of ρ^{SD} into those from the $2a_1$ σ orbital and from the $1b_2$ π orbital. It is interesting to compare the algebraic signs and magnitudes of these contributions with those of ρ^{SD} (the third column). The spin polarization terms are also divided into those contributing from the σ and π orbitals in the seventh and the eighth columns. Their contribution to the isotropic hfs constant is large while those to the anisotropic hfs constants are small as mentioned before. The last three columns list the available experimental data for CD_2, though their algebraic signs are not determined by an EPR experiment. The magnitudes of our predicted hfs constants well compare with those observed.

We list in Table 6 our prediction of the hfs constants in CF_2 and CHF for which no experimental data are available. It is hoped that our predictions will serve as a guide in future experimental analyses for these radicals.

Appendix A. The MO and AO Spin Density Operators

The MO spin density operators over the states given in Eqs. 23—26 of the text are expressed in terms of the transition-operators $\hat{P}_{ij} \equiv |\phi_i\rangle\langle\phi_j|$ as follows:

$$\hat{\rho}(\Psi^M_G; \Psi^M_G) = \frac{1}{2}(\hat{P}_{mm} + \hat{P}_{nn}),$$

$$\hat{\rho}(\Psi^M_{i\to m}; \Psi^M_G) = -\frac{1}{2}\hat{P}_{im},$$

$$\hat{\rho}(\Psi^M_{m\to k}; \Psi^M_G) = \frac{1}{2}\hat{P}_{mk},$$

$$\hat{\rho}(\Psi^M_{i\to k}(\mathrm{A}); \Psi^M_G) = 0,$$

$$\hat{\rho}(\Psi^M_{i\to k}(\mathrm{B}); \Psi^M_G) = \hat{\rho}(\Psi^M_{i\to k}(\mathrm{C}); \Psi^M_G) = -(1/\sqrt{6})\hat{P}_{ik},$$

$$\hat{\rho}(\Psi_1{}^{(\mathrm{m})}; \Psi^M_G) = -\hat{\rho}(\Psi_2{}^{(\mathrm{m})}; \Psi^M_G) = -\frac{1}{2}\hat{P}_{ik},$$

$$\hat{\rho}(\Psi_3{}^{(\mathrm{m})}; \Psi^M_G) = \hat{\rho}(\Psi_3{}^{(\mathrm{n})}; \Psi^M_G) = 0.$$

The AO spin density matrix $\bar{\boldsymbol{\rho}}$ for the resultant state Ψ^M_T is easily obtained by making use of Eq. 10 of the text, whose element is

$$\bar{\rho}_{rs} = \frac{1}{2}(C_{rm}C^*_{sm} + C_{rn}C^*_{sn}) + \sum_{i}^{\substack{\text{doubly}\\ \text{occupied}}} \sum_{k}^{\text{vacant}} (1/\sqrt{6})(\lambda^{(\mathrm{m})}_{ik} + \lambda^{(\mathrm{n})}_{ik})(C_{ri}C^*_{sk} + C_{rk}C^*_{si}),$$

where λ_{ik}'s are given in Eq. 38 of the text.

Appendix B. Analytical Derivation of Dipolar Integrals

The formulas for the dipolar integrals over AO's which are needed in the evaluation of anisotropic hfs tensors are obtained by the use of the method of McConnell and Strathdee[26] with the corrections of Pitzer, Kern, and Lipscomb.[27]

In the case when the Slater-type AO's are centered at nucleus N, the evaluation of dipolar integrals is straightforward:

$$t_{ij}(2p_k, 2p_l) = (c/120)\{2\delta_{ij}\delta_{kl} - 3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\},$$

where $c = (Z/a_0)^3$, a_0 being the first Bohr radius, and all the dipolar integrals over spherically symmetric AO's vanish. Constant c in the above equation for the improved one-center dipolar integrals over the Löwdin SCF AO's is[13]

$$c = \frac{\sum_{k,k'} B_k B_{k'}(b_k + b_{k'})^{-2}}{\sum_{k,k'} B_k B_{k'}(b_k + b_{k'})^{-5} a_0{}^3},$$

TABLE A1. FORMULAS OF DIPOLAR INTEGRALS INVOLVING 1s, 2s, 2p STO'S WHEN NUCLEUS N LIES ON THE z AXIS

$\chi_r\chi_s$	t_{xx}	t_{yy}	t_{zz}	t_{xy}	t_{xz}	t_{yz}
1s1s	B_{1s}	B_{1s}	$-2B_{1s}$	0	0	0
2s2s	B_{2s}	B_{2s}	$-2B_{2s}$	0	0	0
2s2p$_x$	0	0	0	0	B_{sx}	0
2s2p$_y$	0	0	0	0	0	B_{sy}
2s2p$_z$	B_{sz}	B_{sz}	$-2B_{sz}$	0	0	0
2p$_x$2p$_y$	0	0	0	B_{xy}	0	0
2p$_x$2p$_z$	0	0	0	0	B_{xz}	0
2p$_y$2p$_z$	0	0	0	0	0	B_{yz}
2p$_x$2p$_x$	B^x_{xx}	B^y_{xx}	B^z_{xx}	0	0	0
2p$_y$2p$_y$	B^x_{yy}	B^y_{yy}	B^z_{yy}	0	0	0
2p$_z$2p$_z$	B_{zz}	B_{zz}	$-2B_{zz}$	0	0	0

$B_{1s}=(1-(4a^3/3+2a^2+2a+1)\exp(-2a))/R^3$

$B_{2s}=(1-(a^5/72+a^4/24+a^3/6+a^2/2+a+1)\exp(-a))/R^3$

$B_{sx}=(15/a-(a^4/8+5a^3/8+5a^2/2+15a/2+15/a)\exp(-a))R^3/\sqrt{3}$

$B_{sy}=B_{sx}$

$B_{sz}=(15/a-(a^5/24+a^4/8+5a^3/8+5a^2/2+15a/2+15+15/a)\exp(-a))/R^3/\sqrt{3}$

$B_{xy}=(-18/a^2+(a^3/8+3a^2/4+3a+9+18/a+18/a^2)\exp(-a))/R^3$

$B_{xz}=(72/a^2-(a^4/8+5a^3/8+3a^2+12a+36+72/a+72/a^2)\exp(-a))/R^3$

$B_{yz}=B_{xz}$

$B^x_{xx}=(1-54/a^2+(a^3/4+7a^2/4+8a+26+54/a+54/a^2)\exp(-a))/R^3$

$B^y_{xx}=(1-18/a^2+(a^2/4+2a+8+18/a+18/a^2)\exp(-a))/R^3$

$B^z_{xx}=-(B^x_{xx}+B^y_{xx})$

$B^x_{yy}=B^y_{xx}$

$B^y_{yy}=B^x_{xx}$

$B^z_{yy}=B^z_{xx}$

$B_{zz}=(1+72/a^2-(a^5/24+a^4/8+3a^3/4+7a^2/2+13a+37+72/a+72/a^2)\exp(-a))/R^3$

TABLE A2. DIPOLAR INTEGRALS WHEN NUCLEUS N LIES AT POINT (X, Y, Z)

$$t_{ij}(1s1s)=(e_{ij}-2u_iu_j)B_{1s}$$

$$t_{ij}(2s2s)=(e_{ij}-2u_iu_j)B_{2s}$$

$$t_{ij}(2s2p_k)=(e_{ik}u_j+e_{jk}u_i)B_{sx}+(e_{ij}-2u_iu_j)u_kB_{sz}$$

$$\begin{aligned} t_{ij}(2p_k2p_l)=&(e_{ik}e_{jl}+e_{il}e_{jk}-2e_{kl}u_iu_j)B^x_{xx}/2\\ &+\{e_{ij}e_{kl}-e_{kl}u_iu_j-(e_{ik}e_{jl}+e_{il}e_{jk})/2\}B^y_{xx}\\ &+(e_{ik}u_ju_l+e_{jl}u_iu_k+e_{il}u_ju_k+e_{jk}u_iu_l)B_{xz}\\ &+(e_{ij}-2u_iu_j)u_ku_lB_{zz}\end{aligned}$$

$$u_x=X/R,\ u_y=Y/R,\ u_z=Z/R,\ e_{ij}=\delta_{ij}-u_iu_j$$

where B_k and b_k are Löwdin's notation and which yields 268.73, 483.42, and 795.75 Å^{-3} for carbon, nitrogen, and oxygen, respectively.

When nucleus N lies on the z axis, the relevant two-center dipolar integrals over the Slater-type AO's, $t_{ij}(\chi_r\chi_s)$, are listed in Table Al, where R is the distance between nucleus N and the atom to which AO's χ_r and χ_s are centered and $a=ZR/a_0$.

The dipolar tensors for which nucleus N lies at point (X, Y, Z) can be obtained by the usual transformation. Table A2 is derived in this way in terms of the terms listed in Table Al.

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