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Spin-Dipolar Contributions to the Nuclear Spin–Spin Coupling Constants of Molecules

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Abstract: This paper presents ab initio coupled Hartree–Fock values for the spin-dipolar contributions, J^2, to the spin–spin coupling constants of molecules. Coupling constants are computed for the molecules hydrogen deuteride, water, hydrogen fluoride, ethane, cyclopropane, and bicyclobutane. These results, along with previously reported values for the orbital contributions, complete the coupled Hartree–Fock calculations of noncontact contributions for a number of spin–spin coupling constants. The problem of calculating spin-dipolar terms using this method in molecules with multiple bonds is discussed. Several estimates of the spin-dipolar terms are given for ethylene, acetylene, and hydrogen cyanide.

I. Introduction

The isotropic nuclear spin–spin coupling constant is the sum of four physically indistinguishable terms:[1] the Fermi contact term J^3, the "diamagnetic" and "paramagnetic" orbital terms J^{1a} and J^{1b}, and the spin-dipolar term J^2. Although the Fermi contact term is usually the most important, recent semiempirical work suggests that this may not always be the case.[2] For this reason it is important to have available ab initio methods for computing the "noncontact" terms.

In previous papers we gave a numerical Monte Carlo method[3] for calculating J^{1a} and an ab initio coupled Hartree–Fock (CHF) procedure[4] for J^{1b}. The present paper describes the application of the CHF method to the spin-dipolar contribution. As the theory has not been fully described for the case of J^2, especially as employed here, and since the dipolar term turns out to be very important in some cases, we will develop the method in moderate detail.

The only previously reported ab initio CHF studies of J^2 were those of Guest et al.[5] for molecules with only one first-row atom, of Ditchfield and Snyder[6] for methyl fluoride, and of Lazzeretti for water[7a] and methanol.[7b] We report here J^2 values for all coupling constants in the molecules hydrogen deuteride, water, hydrogen fluoride, ethane, cyclopropane, and bicyclobutane. The treatment of molecules containing multiple bonds presents difficulties for the CHF method and new methods of calculation will be required. A discussion of this point is given later in the paper.

II. Theory

The contribution $J_{AB}{}^2$ for the nuclei A and B is obtained in the Ramsey theory from the energy bilinear in the perturbations H_A and H_B:

$$J_{AB}{}^2 = (-8\beta^2\hbar^2\gamma_A\gamma_B/3h)\sum_m \langle 0|\sum_k \mathbf{h}_A(k)|m\rangle\cdot \langle m|\sum_{k'}\mathbf{h}_B(k')|0\rangle(E_m - E_0)^{-1} \quad (1)$$

where $|0\rangle$ and $|m\rangle$ are the ground-state and triplet excited state wave functions, respectively, for the $2n$-electron systems. The perturbations are of the form

$$H_A = 2\beta\hbar\gamma_A\sum_k^{2n}[3r_{kA}{}^{-5}(\mathbf{s}_k\cdot\mathbf{r}_{kA})\mathbf{r}_{kA} - \mathbf{s}_k r_{kA}{}^{-3}] \equiv 2\beta\hbar\gamma_A\sum_k \mathbf{h}_A(k) \quad (2)$$

where

$$\mathbf{h}_A(k) = \mathbf{i}h_A{}^x(k) + \mathbf{j}h_A{}^y(k) + \mathbf{k}h_A{}^z(k) \quad (3)$$

In the coupled Hartree–Fock method we employ as an *ansatz* the lowest energy $2n$-electron Slater determinant of molecular orbitals self-consistent in the external perturbation $\mathbf{h}_A$, its effect then being sensed by $\mathbf{h}_B$. In this approximation $J_{AB}{}^2$ is given by

$$J_{AB}{}^2 = (-8\beta^2\hbar^2\gamma_A\gamma_B/3h)\sum_{k=1}^{n}[\langle\phi_k\alpha|\mathbf{h}_B|\cdot\phi_{k\alpha}{}^{(1)}\rangle + \langle\phi_k\beta|\mathbf{h}_B|\cdot\phi_{k\beta}{}^{(1)}\rangle] \quad (4)$$

Here, $\phi_k\alpha$ and $\phi_k\beta$ are the ordinary zeroth-order molecular orbitals of closed-shell Hartree–Fock theory in the absence of the nuclear spin perturbations and $\phi_k\alpha^{(1)}$ and $\phi_k\beta^{(1)}$ are the corresponding first-order vector corrections to the external perturbation $\mathbf{h}_A$, e.g.

$$\phi_k\alpha^{(1)} = \mathbf{i}\phi_{k\alpha x} + \mathbf{j}\phi_{k\alpha y} + \mathbf{k}\phi_{k\alpha z} \quad (5)$$

The components $\phi_{k\alpha p}$ for $p = x, y, z$ are solutions to the set of coupled equations

$$(h_0 - e_k)\phi_{k\alpha p} + (2J^p + K^p)\phi_k\alpha = (\langle\phi_k\alpha|h_A{}^p|\phi_k\alpha\rangle - h_A{}^p)\phi_k\alpha \quad (6)$$

$$J^p = \sum_{j=1}^{n}\int Re[\phi_{j\alpha p}(2)^*\phi_j(2)\alpha(2) + \phi_{j\beta p}(2)^*\phi_j(2)\beta(2)]r_{12}{}^{-1}\,d\tau_2\,d\sigma_2$$

$$K^p = -\sum_{j=1}^{n}\int[\phi_{j\alpha p}(2)^*\phi_j(1)\alpha(1) + \phi_j(2)\alpha(2)\phi_{j\alpha p}(1) + \phi_{j\beta P}(2)^*\phi_j(1)\beta(1)]r_{12}{}^{-1}\,d\tau_2\,d\sigma_2\,P_{12}$$

The eigenvalue of ϕ_k corresponding to the zeroth-order Hamiltonian h_0 is e_k. A similar equation holds for $\phi_{k\beta p}$.

Several relationships exist between parts of the components of $\phi_k\alpha^{(1)}$ and $\phi_k\beta^{(1)}$ which serve to reduce the amount of computation required to solve eq 6. To see this consider the functions $\mathbf{h}_A\alpha$ and $\mathbf{h}_A\beta$. Suppressing the labels k and A we have

$$\mathbf{h}\alpha = (\hbar r^{-5}/2)\{\mathbf{i}[3xz\alpha + (3x^2 - r^2 + 3xyi)\beta] + \mathbf{j}[3yz\alpha + (3xy + (3y^2 - r^2)i)\beta] + \mathbf{k}[(3z^2 - r^2)\alpha + (3xz + 3yzi)\beta]\} \quad (7a)$$

and

$$\mathbf{h}\beta = (\hbar r^{-5}/2)\{\mathbf{i}[(3x^2 - r^2 - 3xyi)\alpha - 3xz\beta] + \mathbf{j}[(3xy - (3y^2 - r^2)i)\alpha - 3yz\beta] + \mathbf{k}[(3xz - 3yzi)\alpha - (3z^2 - r^2)\beta]\} \quad (7b)$$

This indicates that the components of $\phi_k\alpha_p$ and $\phi_k\beta_p$ can be written in terms of the real-valued functions $u_k{}^{pq}$ as

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$$\begin{aligned}\phi_{k\alpha x} &= u_k^{xz}\alpha + (u_k^{xx} + iu_k^{xy})\beta \\ \phi_{k\beta x} &= (u_k^{xx} - iu_k^{xy})\alpha - u_k^{xz}\beta \\ \phi_{k\alpha y} &= u_k^{yz}\alpha + (u_k^{xy} + iu_k^{yy})\beta \\ \phi_{k\beta y} &= (u_k^{xy} - iu_k^{yy})\alpha - u_k^{yz}\beta \\ \phi_{k\alpha z} &= u_k^{zz}\alpha + (u_k^{xz} + iu_k^{yz})\beta \\ \phi_{k\beta z} &= (u_k^{xz} - iu_k^{yz})\alpha - u_k^{zz}\beta\end{aligned} \tag{8}$$

which satisfy the differential equations

$$(h_0 - e_k)u_k^{pq} - \sum_{j=1}^{n}\int [u_j^{pq}(2)\phi_k(2)\phi_j(1) + \phi_j(2)\phi_k(2)u_j^{pq}(1)]r_{12}^{-1}\,\mathrm{d}\tau_2 = [\langle\phi_k|\mathrm{O}_{pq}^{\mathrm{A}}(1)|\phi_k\rangle - \mathrm{O}_{pq}^{\mathrm{A}}(1)]\phi_k(1) \tag{9}$$

The perturbing operators $\mathrm{O}_{pq}^{\mathrm{A}}(k)$ are defined as

$$\begin{aligned}\mathrm{O}_{pq}^{\mathrm{A}}(k) &= 3r_{k\mathrm{A}}^{-5}p_{k\mathrm{A}}q_{k\mathrm{A}},\ p_{k\mathrm{A}} \neq q_{k\mathrm{A}} \\ &= r_{k\mathrm{A}}^{-5}(3p_{k\mathrm{A}}^2 - r_{k\mathrm{A}}^2),\ p_{k\mathrm{A}} = q_{k\mathrm{A}}\end{aligned} \tag{10}$$

It can be seen that there are a total of six partial differential equations to be solved, one for each of the unique Cartesian products. Each has self-consistency corrections arising solely from the exchange operator. Since only the α part of $\phi_{j\alpha p}$ and the β part of $\phi_{j\beta p}$ survive the spin integrations in eq 6 and since they are equal and opposite, the Coulomb contribution vanishes.

In terms of the u_k^{pq}, J_{AB}^2 is given by

$$J_{\mathrm{AB}}^2 = (-16\beta^2\hbar^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}/3h) \sum_{k=1}^{n} [\sum_{p}\langle\phi_k|\mathrm{O}_{pp}^{\mathrm{B}}|u_k^{pp}\rangle + \sum_{q\neq p}\langle\phi_k|\mathrm{O}_{pq}^{\mathrm{B}}|u_k^{pq}\rangle] \tag{11}$$

III. Implementation

The unperturbed real spatial molecular orbitals, n of which are doubly occupied, are expanded in a basis set of N Gaussian functions, furnishing $N - n$ unoccupied spatial orbitals. In terms of these

$$u_k^{pq} = \sum_{s=n+1}^{N} \phi_s C_{sk}^{pq} \tag{12}$$

which on insertion into eq 9 results in the set of $(N - n)n$ algebraic equations

$$\sum_{t=n+1}^{N}\sum_{j=1}^{n}\{(e_j - e_t)\delta_{st}\delta_{kj} + \langle t(1)j(1)|r_{12}^{-1}|s(2)k(2)\rangle + \langle t(1)s(1)|r_{12}^{-1}|j(2)k(2)\rangle\}C_{tk}^{pq} = h_{sj}^{pq} \tag{13}$$

Here

$$h_{sj}^{pq} = \langle\phi_s|\mathrm{O}_{pq}^{\mathrm{A}}|\phi_j\rangle$$

When the $n(N - n) \times n(N - n)$ matrix, whose sj,tk element is the curly bracket of eq 13, is small enough to be inverted, the algebraic equations need not be solved iteratively and problems of convergence are thereby avoided. Also in that case, all six inhomogeneous equations can be solved by matrix multiplication using the same inverse matrix, which is independent of p and q.[8] Only cyclopropane and bicyclobutane were too large for matrix inversion.

Since the unperturbed molecular orbitals are expanded in an atomic orbital basis, integrals of the operators $\mathrm{O}_{pp}^{\mathrm{A}}$ and $\mathrm{O}_{pq}^{\mathrm{A}}$ over Gaussian basis functions were required. For the former we used the formulas of Matsuoka[9] with the minor revisions given in the Appendix. Expressions for integrals over $\mathrm{O}_{pq}^{\mathrm{A}}$ were derived in the present work and they are also contained in the Appendix.

Most of the calculations of the spin-dipolar terms were made with a contracted Gaussian 6-31G basis set;[10] however, in some cases larger basis sets were employed as well. For HD we used the 10s5p uncontracted Gaussian basis set of Schulman and Kaufman[11] which had been used previously for calculations of J^{1a}, J^{1b}, and J^3 in HD.

Table I. One-Bond Coupled Hartree-Fock Values[a] of J_{AB}^2 and J_{AB}^{1b} (Hz)

$^1J_{\mathrm{AB}}$	molecule	J_{AB}^2	J_{AB}^{1b}	exptl J_{AB}[b]
$^1J_{\mathrm{HD}}$	hydrogen deuteride	0.475	0.776	+42.94, 42.7[c]
$^1J_{\mathrm{CH}}$	ethane	−0.2	1.2	+125.0
	cyclopropane	−0.1	0.8	+162[d]
	bicyclobutane (C_1H_b)	0.2	0.4	+205[d]
	bicyclobutane (C_2H_x)	0.2	0.7	+153[d]
	bicyclobutane (C_2H_n)	0.1	0.6	+169[d]
$^1J_{\mathrm{CC}}$	ethane	1.0	0.2	+34.6
	cyclopropane	−0.4	−0.7	+12.4[e]
	bicyclobutane (C_1C_2)	−0.5	−1.3	+21.0[f]
	bicyclobutane (C_1C_3)	−1.5	−0.9	[g]
$^1J_{\mathrm{HF}}$	hydrogen fluoride	−19.3 (−24.2)	191.5	+530
$^1J_{\mathrm{OH}}$	water	0.7	−11.0	−79

[a] Values of the spin-dipolar and orbital contributions to spin-spin coupling constants obtained by the coupled Hartree-Fock method in the 6-31G basis set. For HD the 10s5p uncontracted set of ref 7 was employed. The value for HF in parentheses was obtained with a 9s5p/4s uncontracted basis set with a hydrogen scale factor of 1.45. [b] Except where noted, references for the experimental values in the table are contained in ref 4. Signs indicated are known or can be reasonably assumed to be known. [c] H. Benoit and P. Piejus, *C. R. Acad. Sci., Ser. B.* 265, 101 (1067); T. F. Wimett, *Phys. Ref. A*, 91, 476 (1953). [d] K. Wüthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys.*, 52, 230 (1970). H_b, H_n, and H_x refer to the bridgehead, endo, and exo protons, respectively. The bridgehead and methylene carbons are C_1 and C_2, respectively. The geometry employed was that of K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 50, 1976 (1969). [e] W. Lüttke, private communication. [f] R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Am. Chem. Soc.*, 94, 997 (1972). [g] The $J_{C_1C_3}$ value for bicyclobutane is unknown; however, see text for a discussion of $J_{C_1C_3}$ in substituted bicyclobutanes.

The hydrogen fluoride J^2 was calculated both in a 6-31G basis ($J_{\mathrm{HF}} = -19.3$ Hz) and the 9s5p/4s uncontracted set with hydrogen scale factor 1.45 used by Guest et al.[5] ($J_{\mathrm{HF}} = -24.2$ Hz). The latter authors obtained $J_{\mathrm{HF}}^2 = -12.6$ Hz with this basis. The reason for this discrepancy is not clear, especially since we were able to duplicate their values for J_{HF}^{1b} and J_{HF}^3 as well as their values for water and the Ditchfield J^2 values for methyl fluoride.[6] One possible difference between the calculations is our use of matrix inversion vs. their iterative solution of the CHF equations.

IV. Discussion of the Coupled Hartree-Fock Results

Table I contains the CHF spin-dipolar values for 13 one-bond coupling constants. Also included are the calculated orbital terms J_{AB}^{1b} and the corresponding experimental values.

The simplest molecule studied is HD, which has served as the traditional test of methods for calculating the Fermi contact term. Experimental values of 42.7[12a] and 42.94 Hz[12b] have been available for some time. However, the noncontact terms were not accurately known and therefore a value of J_{HD}^3 derived from experiment was not available for comparison. From Table I it can be seen that $J_{\mathrm{HD}}^2 = 0.475$ Hz or 1% of the total. Using our previous values, $J_{\mathrm{HD}}^{1a} = -0.366$[3] and $J_{\mathrm{HD}}^{1b} = 0.766$ Hz,[4b] we find that the noncontact terms sum to 0.885 Hz. Accurate Fermi contact calculations should therefore furnish between 41.8 and 42.1 Hz.[13] We

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Table II. Hartree-Fock Values[a] of ${}^nJ_{AB}{}^2$ and ${}^nJ_{AB}{}^{1b}$ where n = 2, 3, 4

${}^nJ_{AB}$	molecule	$J_{AB}{}^2$	$J_{AB}{}^{1b}$	J_{AB} exptl[b]
${}^2J_{HH}$	water	1.6	3.4	7.2
	ethane	0.5	1.0	
	cyclopropane	0.4	1.1	−4.34[c]
	bicyclobutane	0.4	1.1	0.4, 0.6[d]
${}^2J_{CH}$	ethane	−0.1	0.2	−4.8
	cyclopropane	−0.1	0.2	
	bicylcobutane (C_1H_b)	−0.1	0.2	3.3[d]
	bicyclobutane (C_1H_x)	−0.2	0.0	3.3[d]
	bicyclobutane (C_1H_n)	0.2	0.2	0.0[d]
	bicyclobutane (C_2H_b)	0.1	0.1	5.3[d]
${}^2J_{CC}$	bicyclobutane	−0.0	−0.2	
${}^3J_{HH}$	ethane (gauche)	0.1	0.2	8.0
	ethane (trans)	0.1	1.0	
	cyclopropane (cis)	0.2	0.1	8.97[c]
	cyclopropane (trans)	0.0	0.9	5.58[c]
	bicyclobutane (H_bH_b)	0.2	0.4	10.4[d]
	bicylcobutane (H_bH_x)	0.1	0.2	2.9[d]
	bicyclobutane (H_bH_n)	−0.0	0.9	1.2[d]
${}^4J_{HH}$	bicyclobutane (H_xH_x)	0.0	0.8	5.9[d]
	bicyclobutane (H_nH_n)	0.0	−0.6	1.1[d]
	bicyclobutane (H_nH_x)	−0.1	0.7	0.6, 0.4[d]

[a] Values of the spin-dipolar and orbital contributions to spin-spin coupling constants obtained by the coupled Hartree-Fock method in a 6-31G basis set. [b] Except where noted, references for the experimental values in the table are given in ref 4. Signs are indicated where they are known. [c] V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, 46, 4165 (1967). [d] K. Wuthrich, S. Meiboom, and L. C. Snyder, *ibid.*, 52, 230 (1970).

should point out that Ishiguro[14] calculated $J_{HD}{}^{1b}$ and $J_{HD}{}^2$ to be 0.3557 and 0.216, respectively. However, his sum-over-states treatment employed only a few intermediate states and is probably less accurate that the present calculation. Armour[15] obtained $J_{HD}{}^2$ = −0.016 Hz in a CI calculation; however, his basis appears to be deficient in π atomic orbitals.

For organic molecules containing single bonds, $J_{CC}{}^2$ is consistently small. One important case which merits special discussion is the C_1C_3 bond of bicyclobutane, the subject of previous theoretical[16] and experimental[17] studies. We obtain $J_{C_1C_3}{}^2 = -1.5$ and $J_{C_1C_3}{}^{1b} = -0.92$ Hz, suggesting noncontact terms of ca. −2.4 Hz (which is about half the semiempirical value, −4.2 Hz[16b]). Experimental values of $J_{C_1C_3}$ in substituted bicyclobutanes range from −5.4 to −17.5 Hz, the reason for the wide latitude being unclear. Since the coupled Hartree-Fock method tends to overestimate the magnitudes of coupling constants, the bicyclobutane noncontact terms are undoubtedly algebraically greater than −2.4 Hz, and the Fermi contact interaction is the dominant term.

Table II contains the CHF results for two-, three-, and four-bond coupling constants in the same set of molecules. Once again, it is apparent that the spin-dipolar term is small compared with experiment in all cases.

V. The Problem of $J_{AB}{}^2$ in Molecules with Multiple Bonds

When we treated molecules with multiple bonds using the CHF method as in the previous sections, very large spin-dipolar terms were obtained. Thus, for acetylene and ethylene the CHF $J_{CC}{}^2$ were found to be comparable in magnitude to the observed coupling constant and the Fermi contact terms, $J_{CC}{}^3$, were even larger than experiment. Moreover, to make matters worse the sign obtained for $J_{CC}{}^3$ of ethylene was negative, which is opposite to experiment.

Table III. Values of ${}^1J_{AB}{}^2$ Obtained with a Modified Equation 13[a,b] (Hz) for Three Multiply Bonded Molecules, Using Two Basis Sets

		$J_{AB}{}^2$	
${}^1J_{AB}$	molecule	6-31G[c]	$10s^56p^3/5s^3$[d]
${}^1J_{CH}$	ethylene	0.10 (−0.41)	−0.12 (−0.19)
	acetylene	0.15 (0.0)	−0.07 (−1.0)
	hydrogen cyanide	0.16 (0.03)	−0.09 (−0.12)
${}^1J_{CC}$	ethylene	0.30 (8.2)	0.25 (2.3)
	acetylene	1.4 (6.8)	1.5 (4.4)
${}^1J_{CN}$	hydrogen cyanide	−0.87 (−5.2)	−0.90 (−2.8)

[a] Uncoupled Hartree-Fock values, obtained by deleting all two-electron integrals from eq 13. [b] Values in parentheses were obtained from eq 13 by retaining only the diagonal two-electron integrals, $k = j$, $s = t$. [c] Reference 10. [d] Reference 20.

The source of these difficulties most probably lies in the triplet instability, or for acetylene the near instability, of the ground-state doubly occupied spin-restricted wave function. Indeed, the square matrix in curly brackets of eq 13, which is used in the CHF calculations for both spin-dipolar and Fermi contact terms, is precisely the matrix whose eigenvalues are used to test for triplet instability.[18] According to a well-known result,[19] triplet instability exists if any of these eigenvalues is negative. Indeed such is the case for ethylene, whose lowest eigenvalues are −0.012 au in the 6-31G basis and −0.009 au in the larger $10s^56p^3/5s^3$ basis of Dunning.[20] (The next higher eigenvalues are +0.30 au in both bases.) For acetylene the lowest eigenvalues are only slightly positive, being +0.01 au, suggesting a near triplet instability in this case. Thus, a major part of the large CHF J_{CC} values obtained can be attributed to the first-order wave function replacing the doubly occupied ground-state wave function with a spin-unrestricted correction. Failure of the CHF method in cases of triplet instability had in fact been anticipated by Guest, Saunders, and Overill.[5]

Given this spin-symmetry dilemma there are at least two alternative estimates of $J_{AB}{}^2$ that we can make for multiply bonded molecules. We can compute the uncoupled Hartree-Fock values of $J_{AB}{}^2$, by deleting from eq 13 all two-electron integrals. These results, which are contained in Table III, suggest the $J_{CC}{}^2$ for ethylene and acetylene and $J_{CN}{}^2$ for hydrogen cyanide are considerably smaller than experiment. The values of $J_{CH}{}^2$ included in Table III are sensitive to the basis set; however, since they are quite small, this is not a critical point.

A second method of avoiding the full CHF calculation is to include in eq 13 only the diagonal two-electron integrals, i.e., $s = t$, $j = k$. The appeal of this procedure is that the matrix in question now has only positive eigenvalues, approximately 0.2 au in size. The results for these modified CHF calculations are given in parentheses in Table III and are probably more reliable than the uncoupled values, which do not include electron correlation. They are probably the best estimates we can give at this time. The most interesting case is $J_{CN}{}^2$ of hydrogen cyanide, which is predicted to be −2.8 Hz in the Dunning basis, approximately 16% of experiment.

As a final point, we might consider the question of singlet instabilities of the ground-state RHF function with respect to the imaginary perturbations used for orbital term J^{1b}. To test for such imaginary singlet instabilities the eigenvalues of interest are those of a matrix similar to that in eq 13 except that now the sign of the integral $\langle t(1)j(1)|r_{12}{}^{-1}|s(2)k(2)\rangle$ is negative.[21] For ethylene, the smallest eigenvalue in the 6-31G basis is +0.25 au with similar positive eigenvalues found for other multiply bonded molecules. Thus, singlet instabilities do not appear to be an inherent problem

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in the calculation of the orbital term J^{1b}.

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Appendix

This appendix is concerned with evaluating integrals of the form $\langle\chi(\mathrm{A},\alpha_1,l_1,m_1,n_1)|\mathrm{O_C}|\chi(\mathrm{B},\alpha_2,l_2,m_2,n_2)\rangle$ where the operator $\mathrm{O_C}$ associated with center C is one of the "diagonal" operators such as $(3z_C{}^2 - r_C{}^2)r_C{}^{-5}$ or a "cross-term" operator such as $3x_Cy_Cr_C{}^{-5}$. For the diagonal operators we use eq 25 of Matsuoka with his denominator corrected to read $t!w!(k - 2t - 2w + 2)!$. Also, in eq 24 π/γ should be changed to $\pi/2\gamma$.

For the cross-term we use the identity

$$3x_Cy_Cr_C{}^{-5} = -(2\pi^2)^{-1}\int k_xk_yk^{-2}e^{i(\mathbf{k}\cdot\mathbf{r}_C)}\,\mathrm{d}k$$

Following procedures similar to those of Matsuoka we obtain

$$\langle\chi_A|3x_Cy_Cr_C{}^{-5}|\chi_B\rangle = \sum_{I,J,K} G_IU_JU_K\pi(2\gamma)^{-1}e^{-\alpha_1\alpha_2AB^2/\gamma}$$

where the *U*'s are defined by Matsuoka and the remaining quantities by ref 22.

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EPR Studies of the Molecular Motion of Nitroxide Radicals in Poly(vinyl alcohol) Gels

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Abstract: Rotational diffusion of several nitroxide radicals in aqueous solution and in poly(vinyl alcohol) (PVA) gels has been studied by the analysis of line width of EPR spectra based on the axially symmetric rotational diffusion model proposed by Freed et al. The pore size dependence of the motion of nitroxide in PVA gel is made clear, that is, (1) the correlation time of rotational diffusion of the solute molecule sharply increases in the limited space of the solution smaller than 50 times the volume of solute molecule, (2) the rotational diffusion is more anisotropic in a smaller pore, (3) the anisotropy of the interaction of the solute molecule with the surrounding molecules also increases in a smaller pore, and (4) the interaction is mainly due to weak hydrogen bonding between the solute molecule and the hydroxy group of the PVA lattice. In general, the physical nature of the system represented by the volume ratio of the space of solution or the pore to the solute molecule primarily determines the rotational motion in a limited space, though the chemical nature of the solute molecules also affects the rotational motion considerably, especially its rate.

Introduction

Molecular motion of solute and solvent molecules in solution has been extensively investigated by various methods of spectroscopy. However, most of those investigations were done under the condition that the solute and the solvent molecules were in free motion in the bulk media. The purpose of the present investigation is to investigate the molecular motion of the solute molecule which is confined in a small pore, which is of current interest in biological reactions and catalytic reactions.[1,2] Recently, it has been shown by one of the present authors (S.F.)[3] that a certain minimum volume of solution is required for the maintenance of the free motion of the solute molecule in the solution, and this minimum volume has been referred to as the critical volume, V_c. The value of V_c for a solute molecule of relatively simple structure, such as the hydrated Cu^{2+} ion or the 2,2,5,5-tetramethyl-3-carbamoylpyrrolidin-1-oxy radical, was found to be about $(20 \pm 5\ \text{Å})^3$. As a matter of course, the size of V_c is expected to depend on the nature of the solute molecules, particularly on the size or on the chemical properties of the solute molecules. Thus, in this paper measurements of the V_c's were carried out for nitroxide radicals of similar size, but with different functional groups. As the media for limiting the space of the solution, different kinds of gel are applicable. for example, the gels of silica, poly(vinyl alcohol) (PVA), polystyrene, and so on. Several spectroscopic investigations can be referred to as the works which have been carried out on the solutions in those media.[1,4–6] In the present investigation PVA gels have been chosen as the media which control the space of the solution. The analysis of EPR spectra based on the model of axially anisotropic rotational diffusion proposed by Freed et al. was carried out.[7,8]

Experimental Section

Nitroxide Radicals. Five nitroxide radicals with different active groups have been used: 2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempo) (I), 2,2,6,6-tetramethylpiperidinolyl-1-oxy (Tempol) (II), 2,2,6,6-tetramethylpiperidonyl-1-oxy (Tempone) (III), and 2,2,5,5-tetramethyl-3-carboxypyrrolidinyl-1-oxy (IV) were synthesized by the methods shown in the literature,[9] and 2,2,5,5-tetramethyl-3-carbamoylpyrrolidinyl-1-oxy (V) was purchased from Aldrich Chemical Co.

PVA Gel. PVA gels were produced by γ-ray irradiation to PVA aqueous solutions. The average distance between the end terminal of PVA molecules, $\langle l\rangle$, may be expressed by eq 1, which has been semi-

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