COUPLING OF NUCLEAR SPINS IN MOLECULES

By D. W. Posener*

[*Manuscript received June* 19, 1957]

Summary

The theory of quadrupole, magnetic dipole, and dipole-dipole interactions of nuclear spins with molecular rotation is generalized for any number of nuclear spins in any free molecule which has no resultant electronic angular momentum.

Calculation of the matrix elements of the Hamiltonian is discussed in detail, and the cases of one and two nuclear spins are dealt with explicitly.

I. Introduction

First-order matrix elements for the coupling of two similar quadrupolar nuclei in a molecule have been derived by Foley (1947) for the diatomic case, and subsequently by Myers and Gwinn (1952) and Robinson and Cornwell (1953) for more general molecules. Cases of grossly unequal coupling have been considered by Bardeen and Townes (1948*a*, 1948*b*) and by Townes and Schawlow (1955, Section 6–6), although the appropriate matrix elements have not been given explicitly.

Bersohn (1950) has given the matrix elements for the quadrupolar coupling of three nuclei, and his methods, which are applicable to any number of nuclei, are described in his thesis (Bersohn 1949).

Recent advances in high-resolution microwave spectroscopy have drawn more attention to the small magnetic interactions of nuclei (White 1955). Gunther-Mohr, Townes, and Van Vleck (1954) and Gordon (1955) have described the coupling of three hydrogen spins and a quadrupolar nucleus (nitrogen) in ammonia; Okaya (1956) has considered C_{2v} molecules with two $\frac{1}{2}\hbar$ off-axis spins and one axial quadrupolar nucleus; and Herrmann (1956) has treated the experimental problems of ND_3 using some theoretical results derived by Hadley (1955), whose work has not been accessible to the present writer. Although these cases are of increasing complexity, symmetry properties of the particular molecular types so far considered help to provide some simplification of the problems, and the works quoted cannot be easily generalized.

In the following account we will deal with an arbitrary free molecule with no resultant electronic angular momentum, but containing n nuclei each possessing spin, and we will give the complete matrix elements of the major interactions. The results are derived for quadrupolar spins, but can be easily specialized to cases where some of the spins are $\frac{1}{2}\hbar$ or zero.

In most problems of practical interest only a very few of the terms given need to be considered because some terms contribute to the energy only in

* Division of Electrotechnology, C.S.I.R.O., University Grounds, Chippendale, N.S.W.

higher order of approximation, while in many cases some of the matrix elements vanish identically because of symmetry properties of the molecule. Because of their wide variety symmetry considerations peculiar to particular types of molecules will not be specially discussed here, although they will usually be of great importance in further simplifying the calculations in a given problem. We refer to some of the papers already quoted for discussions of this kind.

The results for one and for two nuclei will be given explicitly as simple applications of the general theory.

II. The Hamiltonian

We assume the molecule to be subject to no external fields and to have no resultant electronic orbital or spin angular momentum, so that electron spins are paired and their effects may usually be neglected (as demonstrated, for instance, by Gunther-Mohr, Townes, and Van Vleck (1954)). In the rigid rotor approximation the Hamiltonian for rotation and for the major spin hyperfine interactions is then (Van Vleck 1951 ; Gunther-Mohr, Townes, and Van Vleck 1954) :

$$\begin{aligned} H=&\sum_g \bar{G}_g(J_g-L_g)^2+\frac{e\mu_N}{c}\sum_k\sum_i r_{ik}^{-3}(\mathbf{r}_i-\mathbf{r}_k)\times\left[\mathbf{v}_i-\left(1+\frac{Z_kM_P}{g_kM_k}\right)\mathbf{v}_k\right]\cdot g_k\mathbf{I}_k \\ &-\frac{e\mu_N}{c}\sum_k\sum_{l\neq k}Z_l r_{kl}^{-3}(\mathbf{r}_k-\mathbf{r}_l)\times\left[\left(1+\frac{Z_kM_P}{g_kM_k}\right)\mathbf{v}_k-\mathbf{v}_l\right]\cdot g_k\mathbf{I}_k \\ &+\mu_N^2\sum_k\sum_{l>k}r_{kl}^{-3}\{g_k\mathbf{I}_k\cdot g_l\mathbf{I}_l-3r_{kl}^{-2}[g_k\mathbf{I}_k\cdot(\mathbf{r}_k-\mathbf{r}_l)][g_l\mathbf{I}_l\cdot(\mathbf{r}_k-\mathbf{r}_l)]\} \\ &+\sum_k\frac{1}{12}\left(2\frac{\partial^2V_k}{\partial z_k'^2}-\frac{\partial^2V_k}{\partial x_k'^2}-\frac{\partial^2V_k}{\partial y_k'^2}\right)\int\rho_k(2z_k'^2-x_k'^2-y_k'^2)\mathrm{d}v_k. \quad \ldots\ (1) \end{aligned}$$

where $\mathbf{J}$ is the total angular momentum exclusive of nuclear spin, $\mathbf{L}$ is the electronic orbital angular momentum, and we measure angular momentum in units of $\hbar$. The $\bar{G}_g$ are rotation constants, with g referring to principal inertial axes x, y, and z fixed in the molecule. The sum over i is over the electrons, whose charges are $-e$ and whose positions and velocities are given by $\mathbf{r}_i$ and $\mathbf{v}_i$ respectively, referred to the molecular centre of mass. Indices k and l are used similarly for the n nuclei, which have magnetic moments $g_k\mu_N$, masses M_k, charges Z_k, spins $\mathbf{I}_k$, and nuclear charge densities ρ_k. The proton mass is M_P, μ_N is the nuclear magneton, c is the velocity of light, and r_{ik} is an abbreviation for $|\mathbf{r}_i-\mathbf{r}_k|$. The electrostatic potential at the kth nucleus due to all molecular charges outside the nuclear region is V_k, and x_k', y_k', and z_k' are coordinates fixed in the kth nucleus with the z_k' direction along the nuclear axis of symmetry.

The first term in the Hamiltonian is the energy of rigid rotation, the second term represents the energy of interaction of nuclear magnetic dipoles with currents due to electron motion, the third term is the energy of interaction of nuclear dipoles with currents due to nuclear motion (molecular rotation), the fourth term is the magnetic dipole-dipole interaction of the nuclei with one another, and the last term is the energy of nuclear quadrupolar interaction with the molecular electrostatic fields.

Although the non-rotating molecule possesses zero total electron orbital angular momentum, rotational interactions excite higher electronic states. When perturbation theory is used to take the more important interactions of these states into account (see, for example, Gunther-Mohr, Townes, and Van Vleck 1954), the effective Hamiltonian for the nuclear spin interactions can be written in the form:

$$\begin{aligned}H=&\sum_k[a'_k(\bar{I}_{kx}J_x+\bar{I}_{ky}J_y+\bar{I}_{kz}J_z)+a_k(2\bar{I}_{kz}J_z-\bar{I}_{kx}J_x-\bar{I}_{ky}J_y)\\&+b_k(\bar{I}_{kx}J_x-\bar{I}_{ky}J_y)+c_k(\bar{I}_{kx}J_y+\bar{I}_{ky}J_x)+d_k(\bar{I}_{kx}J_z+\bar{I}_{kz}J_x)\\&+e_k(\bar{I}_{ky}J_z+\bar{I}_{kz}J_y)]+\sum_k\sum_{l>k}[\alpha_S^{(kl)}(2\bar{I}_{kz}\bar{I}_{lz}-\bar{I}_{kx}\bar{I}_{lx}-\bar{I}_{ky}\bar{I}_{ly})\\&+\beta_S^{(kl)}(\bar{I}_{kx}\bar{I}_{lx}-\bar{I}_{ky}\bar{I}_{ly})+\gamma_S^{(kl)}(\bar{I}_{kx}\bar{I}_{ly}+\bar{I}_{ky}\bar{I}_{lx})\\&+\delta_S^{(kl)}(\bar{I}_{kx}\bar{I}_{lz}+\bar{I}_{kz}\bar{I}_{lx})+\varepsilon_S^{(kl)}(\bar{I}_{ky}\bar{I}_{lz}+\bar{I}_{kz}\bar{I}_{ly})]\\&+\sum_k[\alpha_k(2\bar{I}_{kz}^2-\bar{I}_{kx}^2-\bar{I}_{ky}^2)+\beta_k(\bar{I}_{kx}^2-\bar{I}_{ky}^2)+\gamma_k(\bar{I}_{kx}\bar{I}_{ky}+\bar{I}_{ky}\bar{I}_{kx})\\&+\delta_k(\bar{I}_{kx}\bar{I}_{kz}+\bar{I}_{kz}\bar{I}_{kx})+\varepsilon_k(\bar{I}_{ky}\bar{I}_{kz}+\bar{I}_{kz}\bar{I}_{ky})]. \quad \ldots\ldots\ldots\ldots \quad (2)\end{aligned}$$

For convenience in calculation everything in equation (2) is referred to the molecule-fixed system of axes, and for consistent commutation relations the spin angular momenta $\mathbf{I}_k$ have been replaced by their reverses $\bar{\mathbf{I}}_k=-\mathbf{I}_k$ (Van Vleck 1951). The coefficients in equation (2) are:

$$\begin{aligned}a'_k&=\tfrac{1}{3}(M_{xx}^{(k)}+M_{yy}^{(k)}+M_{zz}^{(k)}),\\a_k&=\tfrac{1}{6}(2M_{zz}^{(k)}-M_{xx}^{(k)}-M_{yy}^{(k)}),\\b_k&=\tfrac{1}{2}(M_{xx}^{(k)}-M_{yy}^{(k)}),\\c_k&=\tfrac{1}{2}(M_{xy}^{(k)}+M_{yx}^{(k)}),\\d_k&=\tfrac{1}{2}(M_{xz}^{(k)}+M_{zx}^{(k)}),\\e_k&=\tfrac{1}{2}(M_{yz}^{(k)}+M_{zy}^{(k)}),\\\alpha_S^{(kl)}&=-\tfrac{1}{2}\mu_N^2g_kg_l[2(r_{kl})_z^2-(r_{kl})_x^2-(r_{kl})_y^2]/r_{kl}^5,\\\beta_S^{(kl)}&=-\tfrac{3}{2}\mu_N^2g_kg_l[(r_{kl})_x^2-(r_{kl})_y^2]/r_{kl}^5,\\\gamma_S^{(kl)}&=-3\mu_N^2g_kg_l(r_{kl})_x(r_{kl})_y/r_{kl}^5,\\\delta_S^{(kl)}&=-3\mu_N^2g_kg_l(r_{kl})_x(r_{kl})_z/r_{kl}^5,\\\varepsilon_S^{(kl)}&=-3\mu_N^2g_kg_l(r_{kl})_y(r_{kl})_z/r_{kl}^5,\\\alpha_k&=\frac{eQ_k}{12I_k(2I_k-1)}(2V_{zz}^{(k)}-V_{xx}^{(k)}-V_{yy}^{(k)}),\\\beta_k&=\frac{eQ_k}{4I_k(2I_k-1)}(V_{xx}^{(k)}-V_{yy}^{(k)}),\\\gamma_k&=\frac{eQ_k}{2I_k(2I_k-1)}V_{xy}^{(k)},\\\delta_k&=\frac{eQ_k}{2I_k(2I_k-1)}V_{xz}^{(k)},\\\varepsilon_k&=\frac{eQ_k}{2I_k(2I_k-1)}V_{yz}^{(k)},\\eQ_k&=\int\rho_k(2z^2-x^2-y^2)\mathrm{d}v_k,\\V_{gg'}^{(k)}&=\frac{\partial^2V_k}{\partial g\partial g'},\end{aligned}$$

$$M_{gg'}^{(k)}=\frac{2e\mu_N g_k \bar{G}_g}{\hbar c}\Big\langle\Big(1+\frac{Z_k M_P}{g_k M_k}\Big)\sum_i r_{ik}^{-3}[\delta_{gg'}(\mathbf{r}_i-\mathbf{r}_k)\cdot\mathbf{r}_k-(\mathbf{r}_i-\mathbf{r}_k)_g(\mathbf{r}_k)_{g'}]$$
$$+\sum_{l\neq k} Z_l r_{kl}^{-3}\Big\{\delta_{gg'}(\mathbf{r}_k-\mathbf{r}_l)\cdot\Big[\Big(1+\frac{Z_k M_P}{g_k M_k}\Big)\mathbf{r}_k-\mathbf{r}_l\Big]$$
$$-(\mathbf{r}_k-\mathbf{r}_l)_g\Big[\Big(1+\frac{Z_k M_P}{g_k M_k}\Big)\mathbf{r}_k-\mathbf{r}_l\Big]_{g'}\Big\}\Big\rangle$$
$$+\frac{2e\mu_N g_k \bar{G}_g}{c}\sum_p{}' \frac{(0\mid L_g\mid p)(p\mid \Pi_{g'}^{(k)}\mid 0)+(0\mid \Pi_{g'}^{(k)}\mid p)(p\mid L_g\mid 0)}{E_0-E_p},$$
$$\Pi_g^{(k)}=\sum_i r_{ik}^{-3}[(\mathbf{r}_i-\mathbf{r}_k)\times\mathbf{v}_i]_g, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

in which $\delta_{gg'}$ is the Kronecker delta, p specifies an excited electronic state of energy E_p, and the last sum indicated in $M_{gg'}^{(k)}$ is to be taken over all values of p except $p=0$. $(r_{kl})_g$ is short for $(\mathbf{r}_k-\mathbf{r}_l)_g$. The functions of $(r_{kl})_g$ and of $V_{gg'}^{(k)}$, together with the other averages shown explicitly here and later, are to be averaged over the ground electronic and vibrational state of the molecule.

In most practical cases a large number of these coefficients vanish because of molecular symmetry, or can be neglected since they contribute to the energy only in higher order.

III. Addition of Angular Momenta

Bersohn (1949), using the tensor procedure of Racah (1942), has discussed a general method for calculating the matrix elements for the quadrupole coupling of a number of nuclei in a molecule. Condon and Shortley (1953) (hereafter referred to as TAS), following Guttinger and Pauli (1931), have derived the matrix elements of two commuting angular momenta. This section will show that the extension of the methods of TAS to any number of commuting angular momenta is not as formidable as it might first appear, and the results are in some cases rather simpler to use than those of Bersohn.

Since the problem of addition of a number of commuting angular momenta is rather general the notation of TAS will be followed as far as possible, with suitable generalizations and with some of the functions introduced by Van Vleck (1951), and as a basis for our subsequent discussion we shall start by reviewing the appropriate results given in TAS.

(a) *Review of TAS Results*

In a representation which diagonalizes the square of the total angular momentum **J** and its component J_Z along some space-fixed Z-axis, the matrix elements of the components of **J** are off-diagonal in the quantum number m only, and are given by TAS, Section 2[3]:

$$\left.\begin{aligned}(\alpha jm\mid J_X\mid \alpha j\, m\pm 1)&=\tfrac{1}{2}f(j,\pm m),\\ (\alpha jm\mid J_Y\mid \alpha j\, m\pm 1)&=\pm\tfrac{1}{2}\mathrm{i}f(j,\pm m),\\ (\alpha jm\mid J_Z\mid \alpha jm)&=m,\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4)$$

where

$$f(j,m)=\sqrt{\{(j-m)(j+m+1)\}}, \qquad \ldots\ldots\ldots\ldots \quad (5)$$

$\mathrm{i}=\sqrt{(-1)}$, and we have used α to represent the totality of unspecified quantum numbers.

If **T** is a vector operator which obeys the commutation rule TAS 8^31, the dependence on m of the components of **T** is given by TAS 9^311:

$$\left.\begin{aligned}
(\alpha jm \mid T_X \mid \alpha' j+1\ m\pm1) &= \mp\tfrac{1}{2}(\alpha j\vdots T\vdots \alpha' j+1)g(j, \mp m-2),\\
(\alpha jm \mid T_X \mid \alpha' j\ m\pm1) &= \tfrac{1}{2}(\alpha j\vdots T\vdots \alpha' j)f(j, \pm m),\\
(\alpha jm \mid T_X \mid \alpha' j-1\ m\pm1) &= \pm\tfrac{1}{2}(\alpha j\vdots T\vdots \alpha' j-1)g(j, \pm m),\\
(\alpha jm \mid T_Y \mid \alpha' j' m') &= \pm\mathrm{i}(\alpha jm \mid T_X \mid \alpha' j' m'),\\
(\alpha jm \mid T_Z \mid \alpha' j+1\ m) &= (\alpha j\vdots T\vdots \alpha' j+1)\sqrt{\{(j+1)^2-m^2\}},\\
(\alpha jm \mid T_Z \mid \alpha' jm) &= (\alpha j\vdots T\vdots \alpha' j)m,\\
(\alpha jm \mid T_Z \mid \alpha' j-1\ m) &= (\alpha j\vdots T\vdots \alpha' j-1)\sqrt{(j^2-m^2)},
\end{aligned}\right\} \quad \ldots\ (6)$$

where

$$g(j, m)=\sqrt{\{(j-m)(j-m-1)\}}, \quad \ldots\ (7)$$

and $(\alpha j\vdots T\vdots \alpha' j')$ is independent of m. The equations (6) show that the matrix of **T** can be factored into submatrices, one of which contains the whole dependence on the quantum number m.

If

$$\mathbf{J}_1+\mathbf{J}_2=\mathbf{J}, \quad \ldots\ (8)$$

and $\mathbf{J}_1$ and $\mathbf{J}_2$ commute, TAS 10^3 shows that the dependence on m of $\mathbf{J}_1$ and $\mathbf{J}_2$ is given by the equations (6), and the submatrices $(j\vdots J_1\vdots j')$ and $(j\vdots J_2\vdots j')$ are as shown in Table 1, in which

$$\left.\begin{aligned}
\varphi(j_1, j) &= -\frac{\sqrt{\{P(j_1, j)Q(j_1, j-1)\}}}{j\sqrt{\{(2j-1)(2j+1)\}}},\\
\theta(j_1, j) &= \frac{R(j_1, j)}{2j(j+1)},
\end{aligned}\right\} \quad \ldots\ (9)$$

and

$$\left.\begin{aligned}
P(j_1, j) &= (j-j_2+j_1)(j+j_2+j_1+1),\\
Q(j_1, j) &= (j_2+j_1-j)(j+j_2-j_1+1),\\
R(j_1, j) &= j(j+1)-j_2(j_2+1)+j_1(j_1+1).
\end{aligned}\right\} \quad \ldots\ (10)$$

Functions of (j_2, j) are obtained by interchanging j_1 and j_2 throughout. Also,

$$\varphi(j_2, j)=\varphi(j_1, j). \quad \ldots\ (11)$$

Here and subsequently we show only two variables (quantum numbers) explicitly since the third is always defined by the coupling scheme (such as equations (8) and (15)); we will use s and t to denote a general pair of such quantum numbers.

For brevity we frequently omit diagonal quantum numbers from the matrix elements.

If **P** is any vector operator which commutes with $\mathbf{J}_1$, but obeys TAS 8^31 with respect to **J**, then by TAS 11^3 the dependence of the components of **P** on m is given by the equations (6), and the dependence of $(\alpha j\vdots P\vdots \alpha' j')$ on j may also be factored out:

$$(\alpha j_2 j\vdots P\vdots \alpha' j_2' j')=(\alpha j_2\vdots P\vdots \alpha' j_2')(j_2 j \mid j_2' j'), \quad \ldots\ (12)$$

where the submatrix $(j_2 j \mid j_2' j')$ is given by Table 2 with s and t replaced by j_2 and j. It will be noticed that $(st \mid s' t')$ is a Hermitian matrix, and this property of the matrices will be used later in other results when for conciseness not all

TABLE 1

THE MATRICES $(j \vdots J_1 \vdots j')$ AND $(j \vdots J_2 \vdots j')$

j'	$j+1$	j	$j-1$
$(j \vdots J_1 \vdots j')$	$-\frac{1}{2}\varphi(j_1, j+1)$	$\theta(j_1, j)$	$-\frac{1}{2}\varphi(j_1, j)$
$(j \vdots J_2 \vdots j')$	$\frac{1}{2}\varphi(j_2, j+1)$	$\theta(j_2, j)$	$\frac{1}{2}\varphi(j_2, j)$

TABLE 2

THE MATRIX $(st \mid s' t')$

s' \ t'	$t+1$	t	$t-1$
$s+1$	$\frac{1}{2}\xi(s+1, t+1)$	$\eta(s+1, t)/2t(t+1)$	$\frac{1}{2}\zeta(s+1, t-1)$
s	$\frac{1}{2}\varphi(s, t+1)$	$\theta(s, t)$	$\frac{1}{2}\varphi(s, t)$
$s-1$	$\frac{1}{2}\zeta(s, t)$	$\eta(s, t)/2t(t+1)$	$\frac{1}{2}\xi(s, t)$

possible matrix elements will be written down explicitly. In Table 2 the new functions are:

$$\left.\begin{aligned} \xi(s, t) &= \frac{\sqrt{\{P(s, t)P(s, t-1)\}}}{t\sqrt{\{(2t-1)(2t+1)\}}}, \\ \eta(s, t) &= \sqrt{\{P(s, t)Q(s, t)\}}, \\ \zeta(s, t) &= -\frac{\sqrt{\{Q(s, t)Q(s, t+1)\}}}{(t+1)\sqrt{\{(2t+1)(2t+3)\}}}. \end{aligned}\right\} \quad \ldots\ldots \quad (13)$$

(*b*) *Matrix Elements of* $\mathbf{J}_k$ *where* $\sum_k \mathbf{J}_k = \mathbf{J}$

We now consider the addition of $n+1$ commuting angular momenta:

$$\sum_{k=0}^{n} \mathbf{J}_k = \mathbf{J}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

and let us add them together one at a time, defining $n-1$ "intermediate" quantum numbers according to

$$\left.\begin{aligned} \mathbf{J}_n + \mathbf{J}_{n-1} &= \mathbf{J}_{n-1, n}, \\ &\cdots\cdots \\ \mathbf{J}_{k+1, n} + \mathbf{J}_k &= \mathbf{J}_{k, n}, \\ &\cdots\cdots \\ \mathbf{J}_{1, n} + \mathbf{J}_0 &= \mathbf{J}, \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (15)$$

where $\mathbf{J}$ can be considered to be short for $\mathbf{J}_{0,n}$. Then, since all the $\mathbf{J}_k$ commute, we can put into equation (**12**)

$$\mathbf{J}_1\mathbf{J}_2\mathbf{J}\mathbf{P}\rightarrow\mathbf{J}_k\mathbf{J}_{k+1,n}\mathbf{J}_{k,n}\mathbf{J}_l \quad (l>k), \quad \ldots\ldots\ldots \quad (16)$$

and it follows that the matrix elements of the components of $\mathbf{J}_k$ are given by the equations (**6**) together with

$$\begin{aligned}&(j_{k,n}\,j_{k-1,n}\ldots j_{1,n}j'\vdots J_k\vdots j'_{k,n}j'_{k-1,n}\ldots j'_{1,n}j')\\ &=(j_{k,n}\vdots J_k\vdots j'_{k,n})(j_{k,n}j_{k-1,n}\mid j'_{k,n}j'_{k-1,n})\ldots(j_{1,n}j\mid j'_{1,n}j'), \quad \ldots \quad (17)\end{aligned}$$

where diagonal quantum numbers (such as $j_{k+1}, j_k, j_{k+1,n}, \ldots$) have been omitted, and the elements $(j_{k,n}j_{k-1,n}\mid j'_{k,n}j'_{k-1,n})$ are given in Table 2.

The factors $(j_{k,n}\vdots J_k\vdots j'_{k,n})$ are obtained from Table 1 on putting

$$\mathbf{J}_1\mathbf{J}_2\mathbf{J}\rightarrow\mathbf{J}_k\mathbf{J}_{k+1,n}\mathbf{J}_{k,n} \quad (k\neq n), \quad \ldots\ldots\ldots\ldots \quad (18)$$

which is consistent with equation (**16**), and are:

$$\left.\begin{aligned}(j_{k,n}\vdots J_k\vdots j_{k,n}+1)&=-\tfrac{1}{2}\varphi(j_k, j_{k,n}+1),\\ (j_{k,n}\vdots J_k\vdots j_{k,n})&=\theta(j_k, j_{k,n}),\\ (j_{k,n}\vdots J_k\vdots j_{k,n}-1)&=-\tfrac{1}{2}\varphi(j_k, j_{k,n}),\end{aligned}\right\} \quad (k\neq n) \quad \ldots\ldots \quad (19)$$

while for $k=n$,

$$\left.\begin{aligned}(j_{n-1,n}\vdots J_n\vdots j_{n-1,n}+1)&=\tfrac{1}{2}\varphi(j_n, j_{n-1,n}+1),\\ (j_{n-1,n}\vdots J_n\vdots j_{n-1,n})&=\theta(j_n, j_{n-1,n}),\\ (j_{n-1,n}\vdots J_n\vdots j_{n-1,n}-1)&=\tfrac{1}{2}\varphi(j_n, j_{n-1,n}).\end{aligned}\right\} \quad (k=n) \quad \ldots\ldots \quad (20)$$

(*c*) *Matrix Elements of* $2\mathbf{J}^2_{k,Z}-\mathbf{J}^2_{k,X}-\mathbf{J}^2_{k,Y}$ *etc.*

If we use the equations (**6**) to express the dependence on m, it turns out that the matrices of $2J^2_{k,Z}-J^2_{k,X}-J^2_{k,Y}$ etc. can also be factored into submatrices:

$$\left.\begin{aligned}(\alpha jm\mid 2J^2_{k,Z}-J^2_{k,X}-J^2_{k,Y}\mid\alpha'j'm')&=(\alpha j\mid\mid J^2_k\mid\mid\alpha'j')(jm\mid\mid j'm')\delta_{m'm},\\ (\alpha jm\mid J^2_{k,X}-J^2_{k,Y}\mid\alpha'j'm')&=(\alpha j\mid\mid J^2_k\mid\mid\alpha'j')(jm\mid\mid j'm')\delta_{m'm\pm2},\\ (\alpha jm\mid J_{k,X}J_{k,Y}+J_{k,Y}J_{k,X}\mid\alpha'j'm')&=\pm\mathrm{i}(\alpha j\mid\mid J^2_k\mid\mid\alpha'j')(jm\mid\mid j'm')\delta_{m'm\pm2},\\ (\alpha jm\mid J_{k,X}J_{k,Z}+J_{k,Z}J_{k,X}\mid\alpha'j'm')&=(\alpha j\mid\mid J^2_k\mid\mid\alpha'j')(jm\mid\mid j'm')\delta_{m'm\pm1},\\ (\alpha jm\mid J_{k,Y}J_{k,Z}+J_{k,Z}J_{k,Y}\mid\alpha'j'm')&=\pm\mathrm{i}(\alpha j\mid\mid J^2_k\mid\mid\alpha'j')(jm\mid\mid j'm')\delta_{m'm\pm1},\end{aligned}\right\}$$

$$\ldots\ldots\ldots\ldots\ldots \quad (21)$$

where $j'=j, j\pm1, j\pm2$, $m'=m, m\pm1, m\pm2$, and $(jm\mid\mid j'm')$ is given in Table 3, from which the elements $(jm\mid\mid j+1m')$ and $(jm\mid\mid j+2m')$ may be obtained by use of the Hermitian property of the matrix.

In conventional notation the matrix elements of the product of two operators are given by

$$(\alpha\mid TU\mid\alpha')=\sum_{\alpha''}(\alpha\mid T\mid\alpha'')(\alpha''\mid U\mid\alpha'). \quad \ldots\ldots\ldots \quad (22)$$

In the submatrices $(\alpha j \,||\, J_k^2 \,||\, \alpha' j')$ the double bar is used as an abbreviation for a special kind of summation which we define by:

$$(\alpha\beta \,||\, TU \,||\, \alpha'\,\beta') = \begin{cases} \sum_{\alpha''} 2(\alpha\beta \mid T \mid \alpha''\beta)(\alpha''\beta \mid U \mid \alpha'\beta) - (\alpha\beta \mid TU \mid \alpha'\beta), \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{if } \beta' = \beta, \\ (\alpha\beta \mid TU \mid \alpha'\,\beta'), \quad \text{if } \beta' \neq \beta. \end{cases} \quad \ldots\ldots\ldots\ldots \quad (23)$$

The double bar is also used in $(jm \,||\, j'\,m')$ because it results from a summation very similar to (23).

TABLE 3

THE MATRIX $(jm \,||\, j'\,m')$

j' \ m'	m	$m \pm 1$	$m \pm 2$
j	$3m^2 - j(j+1)$	$\frac{1}{2}(2m \pm 1) f(j, \pm m)$	$\frac{1}{2} f(j, \pm m) f(j, \pm m + 1)$
$j-1$	$3m\sqrt{(j^2 - m^2)}$	$\frac{1}{2}(j \pm 2m + 1) g(j, \pm m)$	$\pm\frac{1}{2} f(j, \pm m) g(j-1, \pm m)$
$j-2$	$3g(j, m) g(j, -m)$	$\pm g(j, \pm m + 1)\sqrt{(j^2 - m^2)}$	$\frac{1}{2} g(j, \pm m) g(j, \pm m + 2)$

With this notation we can write generally:

$$\begin{aligned} &(j_{k,n} j_{k-1,n} \ldots j_{1,n} jm \mid 2J_{k,Z}^2 - J_{k,X}^2 - J_{k,Y}^2 \mid j'_{k,n} j'_{k-1,n} \ldots j'_{1,n} j'\, m') \\ &\quad = (j_{k,n} j_{k-1,n} \ldots j_{1,n} j \,||\, J_k^2 \,||\, j'_{k,n} j'_{k-1,n} \ldots j'_{1,n} j')(jm \,||\, j'\, m')\delta_{m'm} \\ &\quad = (j_{k,n} j_{k-1,n} \ldots j_{1,n} \,||\, J_k^2 \,||\, j'_{k,n} j'_{k-1,n} \ldots j'_{1,n})(j_{1,n} j \,||\, j'_{1,n} j')(jm \,||\, j'\, m')\delta_{m'm} \\ &\quad = (j_{k,n} \,||\, J_k^2 \,||\, j'_{k,n})(j_{k,n} j_{k-1,n} \,||\, j'_{k,n} j'_{k-1,n}) \ldots (j_{1,n} j \,||\, j'_{1,n} j')(jm \,||\, j'\, m')\delta_{m'm}, \end{aligned}$$
$$\ldots\ldots\ldots\ldots \quad (24)$$

and similarly, from the equations (21), for the other functions of the components of $\mathbf{J}_k$. The elements of the matrices $(j_{k,n} j_{k-1,n} \,||\, j'_{k,n} j'_{k-1,n})$ etc. are given in Table 4, in which

$$\left.\begin{aligned} \rho(s,t) &= \{3R(s,t)[R(s,t)-1] - 4s(s+1)t(t+1)\}\Phi(t), \\ \chi(s,t) &= [\theta(s,t) + \theta(s,t-1)]\varphi(s,t), \\ \psi(s,t) &= \tfrac{1}{2}\varphi(s,t)\varphi(s,t-1), \\ \Phi(t') &= \begin{cases} [t(t+2)]^{-1}, & \text{if } t' = t+1, \\ [2t(t+1)(2t-1)(2t+3)]^{-1}, & \text{if } t' = t, \\ [(t-1)(t+1)]^{-1}, & \text{if } t' = t-1. \end{cases} \end{aligned}\right\} \quad \ldots\ldots \quad (25)$$

Using equations (19), (20), and (23),

$$\left.\begin{aligned} (j_{k,n} \,||\, J_k^2 \,||\, j_{k,n}) &= \rho(j_k, j_{k,n}), \\ (j_{k,n} \,||\, J_k^2 \,||\, j_{k,n} - 1) &= -\tfrac{1}{2}\chi(j_k, j_{k,n}), \quad (k \neq n) \\ (j_{k,n} \,||\, J_k^2 \,||\, j_{k,n} - 2) &= \tfrac{1}{2}\psi(j_k, j_{k,n}), \end{aligned}\right\} \quad \ldots\ldots \quad (26)$$

and

$$\left.\begin{aligned}(j_{n-1,n} \,||\, J_n^2 \,||\, j_{n-1,n}) &= \rho(j_n, j_{n-1,n}),\\ (j_{n-1,n} \,||\, J_n^2 \,||\, j_{n-1,n}-1) &= \tfrac{1}{2}\chi(j_n, j_{n-1,n}), \quad (k=n)\\ (j_{n-1,n} \,||\, J_n^2 \,||\, j_{n-1,n}-2) &= \tfrac{1}{2}\psi(j_n, j_{n-1,n}).\end{aligned}\right\} \quad .. \quad (27)$$

The simplification of some of the algebra occurring in the calculations leading to equation (**24**) is assisted by use of the identity (**11**) together with :

$$\left.\begin{aligned}P(s+q, t) &= P(s, t+q),\\ Q(s+q, t) &= Q(s, t-q),\\ \rho(s, t) &= \theta^2(s, t) - \tfrac{1}{4}\varphi^2(s, t+1) - \tfrac{1}{4}\varphi^2(s, t)\\ &= -\eta^2(s+1, t)/4t^2(t+1)^2 + \tfrac{1}{4}\xi^2(s+1, t+1) + \tfrac{1}{4}\zeta^2(s+1, t-1)\\ &= -\eta^2(s, t)/4t^2(t+1)^2 + \tfrac{1}{4}\xi^2(s, t) + \tfrac{1}{4}\zeta^2(s, t).\end{aligned}\right\} \quad ..... \quad (28)$$

TABLE 4

THE MATRIX $(st \,||\, s' t')$

s' \ t'	t	$t-1$	$t-2$
$s+2$	$3\eta(s+1, t)\eta(s+2, t)\Phi(t)$	$\tfrac{1}{2}\zeta(s+2, t-1)\eta(s+1, t)\Phi(t-1)$	$\tfrac{1}{4}\zeta(s+1, t-1)\zeta(s+2, t-2)$
$s+1$	$3\eta(s+1, t)[R(s, t)+s]\Phi(t)$	$\tfrac{1}{2}\zeta(s+1, t-1)[R(s, t)+s(t+1)]\Phi(t-1)$	$\tfrac{1}{4}\varphi(s, t)\zeta(s+1, t-2)$
s	$\rho(s, t)$	$\tfrac{1}{2}\chi(s, t)$	$\tfrac{1}{2}\psi(s, t)$
$s-1$	$3\eta(s, t)[R(s-1, t)+(s-1)]\Phi(t)$	$\tfrac{1}{2}\xi(s, t)[R(s, t)-(s+1)(t+1)]\Phi(t-1)$	$\tfrac{1}{4}\varphi(s, t)\xi(s, t-1)$
$s-2$	$3\eta(s, t)\eta(s-1, t)\Phi(t)$	$\tfrac{1}{2}\xi(s, t)\eta(s-1, t-1)\Phi(t-1)$	$\tfrac{1}{4}\xi(s, t)\xi(s-1, t-1)$

(*d*) *Matrix Elements of* $2\mathrm{J_{k,Z}J_Z - J_{k,X}J_X - J_{k,Y}J_Y}$ *etc.*

Using the matrix elements (**4**) and (**17**), it follows easily that

$$\begin{aligned}&(j_{k,n}j_{k-1,n} \ldots j_{1,n}jm \mid 2J_{k,Z}J_Z - J_{k,X}J_X - J_{k,Y}J_Y \mid j'_{k,n}j'_{k-1,n} \ldots j'_{1,n}j'\, m')\\ &= (j_{k,n}j_{k-1,n} \ldots j_{1,n}j \,\vdots\, J_k \,\vdots\, j'_{k,n}j'_{k-1,n} \ldots j'_{1,n}j')(jm \,||\, j'\, m')\delta_{m'm}\\ &= (j_{k,n} \,\vdots\, J_k \,\vdots\, j'_{k,n})(j_{k,n}j_{k-1,n} \mid j'_{k,n}j'_{k-1,n}) \ldots (j_{1,n}j \mid j'_{1,n}j')(jm \,||\, j'\, m')\delta_{m'm},\end{aligned}$$

..... (**29**)

with the factors already defined, and with $j'_{k,n} = j_{k,n}, j_{k,n} \pm 1$, etc.

The other functions of the components of $\mathbf{J}_k$ have matrix elements differing only in their dependence on j and m, as in equation (**21**).

(*e*) *Matrix Elements of* $2\mathrm{J_{k,Z}J_{l,Z} - J_{k,X}J_{l,X} - J_{k,Y}J_{l,Y}}$ *etc.* (l>k)

These cross-product terms have matrix elements of the form

$$\begin{aligned}&(j_{l,n} \ldots j_{k,n} \ldots jm \mid 2J_{k,Z}J_{l,Z} - J_{k,X}J_{l,X} - J_{k,Y}J_{l,Y} \mid j'_{l,n} \ldots j'_{k,n} \ldots j'\, m')\\ &= (j_{l,n} \ldots j_{k,n} \ldots j \,||\, J_k J_l \,||\, j'_{l,n} \ldots j'_{k,n} \ldots j')(jm \,||\, j'\, m')\delta_{m'm}\\ &= (j_{l,n} \,\vdots\, J_l \,\vdots\, j'_{l,n})(j_{l,n}j_{l-1,n} \mid j'_{l,n}j'_{l-1,n}) \ldots (j_{k,n} \,\vdots\, J_k \,\vdots\, j'_{k,n}) \times\\ &\quad (j_{k,n}j_{k-1,n} \,||\, j'_{k,n}j'_{k-1,n}) \ldots (j_{1,n}j \,||\, j'_{1,n}j')(jm \,||\, j'\, m')\delta_{m'm}. \quad .. \quad (30)\end{aligned}$$

In the particular case $k=n-1$ and $l=n$ we get

$$(j_{n-1,n}\ldots j_{1,n}jm \mid 2J_{n-1,Z}J_{n,Z}-J_{n-1,X}J_{n,X}-J_{n-1,Y}J_{n,Y} \mid j'_{n-1,n}\ldots j'_{1,n}j'\,m')$$
$$=(j_{n-1,n}\,||\,J_{n-1}J_n\,||\,j'_{n-1,n})(j_{n-1,n}j_{n-2,n}\,||\,j'_{n-1,n}j'_{n-2,n})\ldots\times$$
$$(j_{1,n}j\,||\,j'_{1,n}j')(jm\,||\,j'\,m')\delta_{m'm}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

with

$$\left.\begin{aligned}(j_{n-1,n}\,||\,J_{n-1}J_n\,||\,j_{n-1,n})&=\theta(j_{n-1},j_{n-1,n})-\rho(j_{n-1},j_{n-1,n}),\\(j_{n-1,n}\,||\,J_{n-1}J_n\,||\,j_{n-1,n}-1)&=-\tfrac{1}{2}\varphi(j_{n-1},j_{n-1,n})+\tfrac{1}{2}\chi(j_{n-1},j_{n-1,n}),\\(j_{n-1,n}\,||\,J_{n-1}J_n\,||\,j_{n-1,n}-2)&=-\tfrac{1}{2}\psi(j_{n-1},j_{n-1,n}).\end{aligned}\right\}$$
$$\ldots\ldots\ldots\ldots \quad (32)$$

When $l=k+1\neq n$ there also results

$$(j_{k+1,n}\ldots jm \mid 2J_{k,Z}J_{k+1,Z}-J_{k,X}J_{k+1,X}-J_{k,Y}J_{k+1,Y} \mid j'_{k+1,n}\ldots j'\,m')$$
$$=(j_{k+1,n}\vdots J_{k+1}\vdots j'_{k+1,n})[j_{k+1,n}j_{k,n}\,||\,j'_{k+1,n}j'_{k,n}]\times$$
$$(j_{k,n}j_{k-1,n}\,||\,j'_{k,n}j'_{k-1,n})\ldots(j_{1,n}j\,||\,j'_{1,n}j')(jm\,||\,j'\,m')\delta_{m'm}, \quad \ldots \quad (33)$$

with $[j_{k+1,n}j_{k,n}\,||\,j'_{k+1,n}j'_{k,n}]$ given in Table 5.

TABLE 5

THE MATRIX $[j_{k+1,n}j_{k,n}\,||\,j'_{k+1,n}j'_{k,n}]$

$j'_{k+1,n}$ \ $j'_{k,n}$	$j_{k,n}$	$j_{k,n}-1$	$j_{k,n}-2$
$j_{k+1,n}+1$	$-\eta(j_{k+1,n}+1, j_{k,n})\times$ $[3R(j_{k+1,n}, j_{k,n})$ $+3(j_{k+1,n}+1)$ $-4j_{k,n}(j_{k,n}+1)]\times$ $\Phi(j_{k,n})$	$\tfrac{1}{2}\zeta(j_{k+1,n}+1, j_{k,n}-1)\times$ $\{1-[R(j_{k+1,n}, j_{k,n})$ $+j_{k+1,n}(j_{k,n}+1)]\times$ $\Phi(j_{k,n}-1)\}$	$-\tfrac{1}{4}\zeta(j_{k+1,n}+1, j_{k,n}-2)\times$ $\varphi(j_{k+1,n}, j_{k,n})$
$j_{k+1,n}$	$\theta(j_{k+1,n}, j_{k,n})$ $-\rho(j_{k+1,n}, j_{k,n})$	$\tfrac{1}{2}\varphi(j_{k+1,n}, j_{k,n})$ $-\tfrac{1}{2}\chi(j_{k+1,n}, j_{k,n})$	$-\tfrac{1}{2}\psi(j_{k+1,n}, j_{k,n})$
$j_{k+1,n}-1$	$-\eta(j_{k+1,n}, j_{k,n})\times$ $[3R(j_{k+1,n}-1, j_{k,n})$ $+3j_{k+1,n}$ $-4j_{k,n}(j_{k,n}+1)]\times$ $\Phi(j_{k,n})$	$\tfrac{1}{2}\xi(j_{k+1,n}, j_{k,n})\times$ $\{1-[R(j_{k+1,n}, j_{k,n})$ $-(j_{k+1,n}+1)(j_{k,n}+1)]$ $\times\Phi(j_{k,n}-1)\}$	$-\tfrac{1}{4}\xi(j_{k+1,n}, j_{k,n})\times$ $\varphi(j_{k+1,n}-1, j_{k,n}-1)$

(f) *Matrix Elements of* $J_{k,X}J_X+J_{k,Y}J_Y+J_{k,Z}J_Z$

This function is the scalar product $\mathbf{J}_k\cdot\mathbf{J}$, and its matrix elements are diagonal in j (TAS Sec. 8[3]). Also,

$$\mathbf{J}_k\cdot\mathbf{J}=3J_{k,Z}J_Z-(2J_{k,Z}J_Z-J_{k,X}J_X-J_{k,Y}J_Y),$$

and it follows from previous results that

$$(j_{k,n}\ldots j_{1,n}jm \mid J_{k,X}J_X+J_{k,Y}J_Y+J_{k,Z}J_Z \mid j'_{k,n}\ldots j'_{1,n}j'\,m')$$
$$=(j_{k,n}\vdots J_k\vdots j'_{k,n})j_{k,n}j_{k-1,n} \mid j'_{k,n}j'_{k-1,n})\ldots(j_{1,n}j \mid j'_{1,n}j')\times j(j+1)\delta_{j'j}\delta_{m'm}.$$
$$\ldots\ldots\ldots\ldots \quad (34)$$

IV. Matrix Elements for One Nuclear Spin

When only one nuclear spin $\mathbf{I}=\mathbf{I}_1$ is present in the molecule we have the coupling scheme

$$\mathbf{J}+\mathbf{I}=\mathbf{F}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (35)$$

or, using the reversed spin angular momentum $\bar{\mathbf{I}}$,

$$\mathbf{F}+\bar{\mathbf{I}}=\mathbf{J}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (36)$$

in which the components of $\mathbf{F}$ and $\bar{\mathbf{I}}$ commute (Van Vleck 1951).

The Hamiltonian (2) is referred to the molecular axis system, and thus (as shown, for example, by Van Vleck (1951)) the results of Section III apply if we change the sign of i and replace m by the quantum number K. Thus our representation may be labelled by the quantum numbers $IJFK$.

We can now use the results of Section III, putting $n=1$ and (cf. equation (18))

$$\mathbf{J}_k\mathbf{J}_{k+1,n}\mathbf{J}_{k,n}\rightarrow\bar{\mathbf{I}}\mathbf{F}\mathbf{J}, \quad \ldots\ldots\ldots\ldots\ldots \quad (37)$$

with $k=0$. Then the matrix elements of the Hamiltonian (2) can be written

$$(JK\mid H\mid J'\,K')=\{(K\mid \mathsf{I}\mid K')(J\parallel \bar{I}^2\parallel J')+(K\mid \mathsf{I}'\mid K')(J\vdots\bar{I}\vdots J')\}(JK\parallel J'\,K'), \quad \ldots\ldots\ldots\ldots \quad (38)$$

where $K'=K, K\pm1, K\pm2$, and $J'=J, J\pm1, J\pm2$. We have introduced the symbols I and I' in equation (38) to distinguish between the various kinds of terms contributing to the Hamiltonian. $(JK\parallel J'\,K')$ is given by Table 6,

Table 6

The matrix $(JK\parallel J'\,K')$

J' \ K'	K	$K\pm1$	$K\pm2$
J	$3K^2-J(J+1)$	$\frac{1}{2}(2K\pm1)f(J,\pm K)$	$\frac{1}{2}f(J,\pm K)f(J,\pm K+1)$
$J-1$	$3K\sqrt{(J^2-K^2)}$	$\frac{1}{2}(J\pm2K+1)g(J,\pm K)$	$\pm\frac{1}{2}f(J,\pm K)g(J-1,\pm K)$
$J-2$	$3g(J,K)g(J,-K)$	$\pm g(J,\pm K+1)\sqrt{(J^2-K^2)}$	$\frac{1}{2}g(J,\pm K)g(J,\pm K+2)$

which is just Table 3 with j and m replaced by J and K. The elements of Table 6 agree with the phase convention of TAS ; if it is required that the matrix elements of this paper be consistent with those of Cross, Hainer, and King (1944), then the column $K\pm1$ would have to be multiplied by $\pm$i, and the column $K\pm2$ by -1. $(J\parallel \bar{I}^2\parallel J')$ and $(J\vdots\bar{I}\vdots J')$ come from equations (26) and (19) respectively, with $j_kj_{k,n}\rightarrow IJ$, and we get the results of Tables 7 and 8. The quantities in Table 7 are the coefficients of the operators in the Hamiltonian, and, since there is only one spin, the subscripts etc. have been dropped. These coefficients are defined

in equation (3). The functions occurring in Table 8 have been defined in equations (9) and (25); explicitly, they are:

$$\left.\begin{aligned}
\rho(I,J)&=\{3R(I,J)[R(I,J)-1]-4I(I+1)J(J+1)\}\Phi(J),\\
\chi(I,J)&=[\theta(I,J)+\theta(I,J-1)]\varphi(I,J),\\
\psi(I,J)&=\tfrac{1}{2}\varphi(I,J)\varphi(I,J-1),\\
\Phi(J)&=[2J(J+1)(2J-1)(2J+3)]^{-1}\\
\varphi(I,J)&=-\frac{\sqrt{\{P(I,J)Q(I,J-1)\}}}{J\sqrt{\{(2J-1)(2J+1)\}}},\\
\theta(I,J)&=\frac{R(I,J)}{2J(J+1)},
\end{aligned}\right\} \quad \ldots\ (39)$$

with

$$\left.\begin{aligned}
P(I,J)&=(J-F+I)(J+F+I+1),\\
Q(I,J)&=(F+I-J)(J+F-I+1),\\
R(I,J)&=J(J+1)-F(F+1)+I(I+1).
\end{aligned}\right\} \quad \ldots\ (40)$$

The above results have already been given by Van Vleck (1951) except that here we have a negative sign in the $(J \mid J\pm1)$ matrix elements; this arises

TABLE 7

THE FACTORS $(K \mid \mathsf{I} \mid K')$ AND $(K \mid \mathsf{I}' \mid K')$

K'	K	$K\pm1$	$K\pm2$
$(K \mid \mathsf{I} \mid K')$	α	$\delta\mp i\varepsilon$	$\beta\mp i\gamma$
$(K \mid \mathsf{I}' \mid K')$	$a+\dfrac{J(J+1)a'}{3K^2-J(J+1)}\delta_{J'J}$	$d\mp ie$	$b\mp ic$

TABLE 8

THE MATRICES $(J \mid\mid \tilde{I}^2 \mid\mid J')$ AND $(J\vdots\bar{I}\vdots J')$

J'	J	$J-1$	$J-2$
$(J \mid\mid \tilde{I}^2 \mid\mid J')$	$\rho(I,J)$	$-\frac{1}{2}\chi(I,J)$	$\frac{1}{2}\psi(I,J)$
$(J\vdots\bar{I}\vdots J')$	$\theta(I,J)$	$-\frac{1}{2}\varphi(I,J)$	0

from our association of I with j_1 rather than with j_2 as in Van Vleck's paper, for we have had to be consistent in our notation (cf equations (16) and (18)) in order to deal with the cross-product terms (Section III (*e*)) correctly.

It will be observed that

$$R(I,J)=2\bar{\mathbf{I}}\cdot\mathbf{J}=-2\mathbf{I}\cdot\mathbf{J}=-C, \quad \ldots\ (41)$$

where C is common notation. Then,

$$\theta(I,J)=\frac{2\bar{\mathbf{I}}\cdot\mathbf{J}}{2J(J+1)}. \quad \ldots\ (42)$$

Also,

$$\rho(I, J)=\frac{4I(2I-1)}{J(J+1)}f(I, J, F), \quad \ldots\ldots\ldots\ldots \quad (43)$$

where $f(I, J, F)$, sometimes called " Casimir's function ", is tabulated by Townes and Schawlow (1955, Appendix I).

For symmetric top molecules the only non-vanishing matrix elements are those diagonal in K, and are:

$$\left.\begin{aligned}(JK \mid H \mid JK)&=[3K^2-J(J+1)]\alpha\rho(I, J)\\&\quad+\{a'J(J+1)+a[3K^2-J(J+1)]\}\theta(I, J),\\(JK \mid H \mid J-1K)&=-\tfrac{3}{2}K\sqrt{J^2-K^2}[\alpha\chi(I, J)+a\varphi(I, J)],\\(JK \mid H \mid J-2K)&=\tfrac{3}{2}g(J, K)g(J, -K)\alpha\psi(I, J).\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (44)$$

In an asymmetric top molecule if only a', a, b, α, and β need be considered (because of molecular symmetry or otherwise), the first-order matrix elements diagonal in J and τ become (Bragg 1948):

$$(J\tau \mid H \mid J\tau)=\alpha_{J,\tau}\rho(I, J)+c_{J,\tau}\theta(I, J), \quad \ldots\ldots\ldots \quad (45)$$

where

$$\left.\begin{aligned}\alpha_{J,\tau}&=\sum_g \chi_{gg}\langle J_g^2\rangle/2I(2I-1),\\c_{J,\tau}&=\sum_g M_{gg}\langle J_g^2\rangle,\\\chi_{gg}&=eQ\langle\partial^2V/\partial g^2\rangle,\\\langle J_a^2\rangle&=\tfrac{1}{2}[J(J+1)+E-(\varkappa+1)\partial E/\partial\varkappa],\\\langle J_b^2\rangle&=\partial E/\partial\varkappa,\\\langle J_c^2\rangle&=\tfrac{1}{2}[J(J+1)-E+(\varkappa-1)\partial E/\partial\varkappa],\end{aligned}\right\} \quad \ldots\ldots \quad (46)$$

in which a, b, and c refer to the principal inertial axes, E is the reduced rigid rotor energy, and $\varkappa$ is the asymmetry parameter.

Usually Laplace's equation $\sum_g \partial^2V/\partial g^2=0$ is applied to eliminate one of the χ_{gg}.

V. Matrix Elements for Two Nuclear Spins

(a) *Matrix Elements for Similar Coupling:* I_2I_1IJFK *Representation*

When the energy of interaction with the rest of the molecule is about the same for each nucleus, the most appropriate coupling scheme is (Foley 1947)

$$\left.\begin{aligned}\mathbf{I}_2+\mathbf{I}_1&=\mathbf{I},\\\mathbf{I}+\mathbf{J}&=\mathbf{F},\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (47)$$

where $\mathbf{I}$ is the total spin angular momentum. The intermediate and total angular momentum quantum numbers cover the ranges

$$\left.\begin{aligned}I&=I_1+I_2,\ I_1+I_2-1,\ \ldots,\ |I_1-I_2|,\\F&=J+I,\ J+I-1,\ \ldots,\ |J-I|.\end{aligned}\right\} \quad \ldots\ldots \quad (48)$$

In general I is not a good quantum number.

By using the reversed spin angular momenta to give

$$\left.\begin{aligned}\bar{\mathbf{I}}_2+\bar{\mathbf{I}}_1&=\bar{\mathbf{I}},\\ \bar{\mathbf{I}}+\mathbf{F}&=\mathbf{J},\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (49)$$

in the molecular representation I_2I_1IJFK, and putting $n=2$ and

$$\mathbf{J}_2\mathbf{J}_1\mathbf{J}_{1,2}\mathbf{J}_0\mathbf{J}\rightarrow\bar{\mathbf{I}}_2\bar{\mathbf{I}}_1\bar{\mathbf{I}}\mathbf{F}\mathbf{J} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (50)$$

in equation (**16**), we can write, similarly to equation (**38**),

$$\begin{aligned}(IJK \mid H \mid I'\,J'\,K')=&[\Sigma_{j=1,2,S}(K \mid \mathsf{I}_j \mid K')(I \mid\mid \bar{I}_j^2 \mid\mid I')(IJ \mid\mid I'\,J')\\ &+\Sigma_{j=1,2}(K \mid \mathsf{I}_j' \mid K')(I\,\dot{:}\,\bar{I}_j\,\dot{:}\,I')(IJ \mid I'\,J')](JK \mid\mid J'\,K'),\\ &\ldots\ldots\ldots\ldots \quad (51)\end{aligned}$$

in which $I'=I, I\pm1, I\pm2$, $J'=J, J\pm1, J\pm2$, and $K'=K, K\pm1, K\pm2$. The matrix $(JK \mid\mid J'\,K')$ has been given in Table 6, and $(K \mid \mathsf{I}_j \mid K')$ and $(K \mid \mathsf{I}_j' \mid K')$

TABLE 9

THE FACTORS $(K \mid \mathsf{I}_j \mid K')$ AND $(K \mid \mathsf{I}_j' \mid K')$

K'	K	$K\pm1$	$K\pm2$
$(K \mid \mathsf{I}_1 \mid K')$	α_1	$\delta_1\mp i\varepsilon_1$	$\beta_1\mp i\gamma_1$
$(K \mid \mathsf{I}_2 \mid K')$	α_2	$\delta_2\mp i\varepsilon_2$	$\beta_2\mp i\gamma_2$
$(K \mid \mathsf{I}_S \mid K')$	α_S	$\delta_S\mp i\varepsilon_S$	$\beta_S\mp i\gamma_S$
$(K \mid \mathsf{I}_1' \mid K')$	$a_1+\dfrac{J(J+1)a_1'}{3K^2-J(J+1)}\delta_{J'J}$	$d_1\mp ie_1$	$b_1\mp ic_1$
$(K \mid \mathsf{I}_2' \mid K')$	$a_2+\dfrac{J(J+1)a_2'}{3K^2-J(J+1)}\delta_{J'J}$	$d_2\mp ie_2$	$b_2\mp ic_2$

TABLE 10

THE MATRICES $(I \mid\mid \bar{I}_j^2 \mid\mid I')$ AND $(I\,\dot{:}\,\bar{I}_j\,\dot{:}\,I')$

I'	I	$I-1$	$I-2$
$(I \mid\mid \bar{I}_1^2 \mid\mid I')$	$\rho(I_1, I)$	$-\frac{1}{2}\chi(I_1, I)$	$\frac{1}{2}\psi(I_1, I)$
$(I \mid\mid \bar{I}_2^2 \mid\mid I')$	$\rho(I_2, I)$	$\frac{1}{2}\chi(I_2, I)$	$\frac{1}{2}\psi(I_2, I)$
$(I \mid\mid \bar{I}_S^2 \mid\mid I')$	$\theta(I_1, I)-\rho(I_1, I)$	$-\frac{1}{2}\varphi(I_1, I)+\frac{1}{2}\chi(I_1, I)$	$-\frac{1}{2}\psi(I_1, I)$
$(I\,\dot{:}\,\bar{I}_1\,\dot{:}\,I')$	$\theta(I_1, I)$	$-\frac{1}{2}\varphi(I_1, I)$	0
$(I\,\dot{:}\,\bar{I}_2\,\dot{:}\,I')$	$\theta(I_2, I)$	$\frac{1}{2}\varphi(I_2, I)$	0

are shown in Table 9, where we have omitted a superscript on the α_S etc. since there is only one dipole-dipole term. The factors $(I \mid\mid \bar{I}_j^2 \mid\mid I')$ (with $\bar{I}_S^2\equiv\bar{I}_1\bar{I}_2$) and $(I\,\dot{:}\,\bar{I}_j\,\dot{:}\,I')$ are obtained from equations (**26**), (**27**), (**32**), (**19**), and (**20**), using (**50**), and are shown in Table 10.

It should be noted that, from equations (**11**) and (**25**),

$$\psi(I_2, I)=\psi(I_1, I). \quad \ldots\ldots\ldots\ldots\ldots \quad (52)$$

$(IJ \,||\, I'J')$ and $(IJ \mid I'J')$ are obtained by putting $st \rightarrow IJ$ in Tables 4 and 2 respectively, and need not be rewritten here.

For an asymmetric top molecule the first-order matrix elements diagonal in J and τ become (cf. equation (**45**)):

$$\left.\begin{aligned}
(IJ\tau \mid H \mid IJ\tau)&=\{\alpha^{(1)}_{J,\tau}\rho(I_1, I)+\alpha^{(2)}_{J,\tau}\rho(I_2, I)+\alpha^{(S)}_{J,\tau}[\theta(I_1, I)-\rho(I_1, I)]\}\rho(I, J)\\
&\quad+[c^{(1)}_{J,\tau}\theta(I_1, I)+c^{(2)}_{J,\tau}\theta(I_2, I)]\theta(I, J),\\
(IJ\tau \mid H \mid I-1J\tau)&=-\{\alpha^{(1)}_{J,\tau}\chi(I_1, I)-\alpha^{(2)}_{J,\tau}\chi(I_2, I)\\
&\quad+\alpha^{(S)}_{J,\tau}[\varphi(I_1, I)-\chi(I_1, I)]\}\tfrac{3}{2}\eta(I, J)[R(I, J)-(I+1)]\Phi(J)\\
&\quad-(c^{(1)}_{J,\tau}-c^{(2)}_{J,\tau})\varphi(I_1, I)\eta(I, J)/4J(J+1),\\
(IJ\tau \mid H \mid I-2J\tau)&=(\alpha^{(1)}_{J,\tau}+\alpha^{(2)}_{J,\tau}-\alpha^{(S)}_{J,\tau})\tfrac{3}{2}\psi(I_1, I)\eta(I, J)\eta(I-1, J)\Phi(J),
\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (53)$$

where

$$\left.\begin{aligned}
\alpha^{(k)}_{J,\tau}&=\Sigma_g \chi^{(k)}_{gg}\langle J_g^2\rangle/2I_k(2I_k-1),\\
\alpha^{(S)}_{J,\tau}&=-(3\mu_N^2 g_1 g_2)[\Sigma_g\langle r_g^2/r^5\rangle\langle J_g^2\rangle-\tfrac{1}{3}\langle r^{-3}\rangle J(J+1)],\\
c^{(k)}_{J,\tau}&=\Sigma_g M^{(k)}_{gg}\langle J_g^2\rangle,\\
\chi^{(k)}_{gg}&=eQ_k\langle \partial^2 V_k/\partial g^2\rangle,
\end{aligned}\right\} \quad \ldots \quad (54)$$

the $\langle J_g^2\rangle$ being defined in equation (**46**) and r standing for r_{12}.

When $I_1=I_2$ the quadrupolar parts of equation (**53**) reduce to the matrix elements of the special cases discussed by Robinson and Cornwell (1953) and by Ramsey (1956, pp. 63, 83).

If the two spins are equal and have equal couplings α_k, the matrix elements of the quadrupole coupling off-diagonal by 1 in I will vanish. If also the spins are symmetrically placed in the molecule, as, for example, in C_{2v} molecules, energy levels with total spin I differing by one unit cannot exist simultaneously for a given symmetry of J and τ, hence the off-diagonal matrix elements $(I \mid I \pm 1)$ can connect only states which also differ in J and/or K. In general, then, if this spin symmetry exists, these $(I \mid I \pm 1)$ contributions to the hyperfine energies will be off-diagonal in the rotation energy and may usually be neglected. However, in a symmetric top molecule levels of different K are degenerate, and the coupling between such states will be first-order, so the splitting may be appreciable, as in the case of ammonia (Gunther-Mohr, Townes, and Van Vleck 1954).

The relative intensities of transitions between hyperfine components described by this coupling scheme can be computed by the method described by Robinson and Cornwell (1953).

The effects of matrix elements off-diagonal in J may be calculated by perturbation theory; in many cases the comparatively large spacings of rotational energies will enable these effects to be neglected.

To first order, only the diagonal elements of the tensor $\chi^{(k)}_{gg'}$ contribute to the energy (Bragg 1948). If the principal axes of this tensor do not coincide with the inertial principal axes x, y, and z, then, in higher order, the off-diagonal elements may have to be taken into account.

(*b*) *Matrix Elements for Non-similar Coupling:* $\mathrm{I_1JF_1I_2FK}$ *Representation*

When one spin ($\mathbf{I}_1$) is more strongly coupled to the rotation than is the other it is usually more convenient to use the coupling scheme (Bardeen and Townes 1948*a*)

$$\left.\begin{aligned}\mathbf{J}+\mathbf{I}_1&=\mathbf{F}_1,\\ \mathbf{F}_1+\mathbf{I}_2&=\mathbf{F},\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (55)$$

with

$$\left.\begin{aligned}F_1&=J+I_1,\ J+I_1-1,\ \ldots,\ |J-I_1|,\\ F&=F_1+I_2,\ F_1+I_2-1,\ \ldots,\ |F_1-I_2|.\end{aligned}\right\} \quad \ldots\ldots \quad (56)$$

In such a representation the general matrix elements of the Hamiltonian become rather more complicated than the previous example, because of the lack of symmetry between $\mathbf{I}_1$ and $\mathbf{I}_2$:

$$\begin{aligned}(F_1JK\,|\,H\,|\,F_1'J'\,K')=&\\ \{(K\,|\,\mathsf{I}_1\,|\,K')(J\,||\,\bar{I}_1^2\,||\,J')+(K\,|\,\mathsf{I}_2\,|\,K')(F_1\,||\,\bar{I}_2^2\,||\,F_1')(F_1J\,||\,F_1'J')&\\ +(K\,|\,\mathsf{I}_S\,|\,K')(F_1\vdots\bar{I}_2\vdots F_1')[F_1J\,||\,F_1'J']+(K\,|\,\mathsf{I}_1'\,|\,K')(J\vdots\bar{I}_1\vdots J')&\\ +(K\,|\,\mathsf{I}_2'\,|\,K')(F_1\vdots\bar{I}_2\vdots F_1')(F_1J\,|\,F_1'J')\}(JK\,||\,J'\,K'),\ \ldots\ldots\ldots&\quad (57)\end{aligned}$$

with $(K\,|\,\mathsf{I}_j\,|\,K')$, $(K\,|\,\mathsf{I}_j'\,|\,K')$, and $(JK\,||\,J'\,K')$ already given in Tables 9 and 6, respectively, $(J\,||\,\bar{I}_1^2\,||\,J')$ and $(F_1\,||\,\bar{I}_2^2\,||\,F_1')$ given in equation (**26**), $(J\vdots\bar{I}_1\vdots J')$ and $(F_1\vdots\bar{I}_2\vdots F_1')$ given by equation (**19**), and $(F_1J\,|\,F_1'J')$, $(F_1J\,||\,F_1'J')$, and $[F_1J\,||\,F_1'J']$ obtained from Tables 2, 4, and 5 respectively.

The matrix elements diagonal in J and τ are (cf. equation (**53**)):

$$\left.\begin{aligned}(F_1J\tau\,|\,H\,|\,F_1J\tau)=&\alpha^{(1)}_{J,\tau}\rho(I_1,J)+\alpha^{(2)}_{J,\tau}\rho(I_2,F_1)\rho(F_1,J)\\ &+\alpha^{(S)}_{J,\tau}\theta(I_2,F_1)[\theta(F_1,J)-\rho(F_1,J)]\\ &+c^{(1)}_{J,\tau}\theta(I_1,J)+c^{(2)}_{J,\tau}\theta(I_2,F_1)\theta(F_1,J),\\ (F_1J\tau\,|\,H\,|\,F_1-1J\tau)=&-\tfrac{3}{2}\alpha^{(2)}_{J,\tau}\chi(I_2,F_1)\eta(F_1,J)[R(F_1-1,J)+(F_1-1)]\Phi(J)\\ &+\tfrac{1}{2}\alpha^{(S)}_{J,\tau}\varphi(I_2,F_1)\eta(F_1,J)[3R(F_1-1,J)+3F_1-4J(J+1)]\Phi(J)\\ &-c^{(2)}_{J,\tau}\varphi(I_2,F_1)\eta(F_1,J)/4J(J+1),\\ (F_1J\tau\,|\,H\,|\,F_1-2J\tau)=&\tfrac{3}{2}\alpha^{(2)}_{J,\tau}\psi(I_2,F_1)\eta(F_1,J)\eta(F_1-1,J)\Phi(J).\end{aligned}\right\}$$

$$\ldots\ldots\ldots\ldots \quad (58)$$

When the coupling of nucleus 2 is much less than that of nucleus 1 it is frequently a good approximation to ignore the matrix elements off-diagonal in F_1, when also the relative intensities of transitions are readily obtained from tables such as in TAS.

VI. Conclusion

It will be apparent that for any number of nuclear spins the matrix elements of the Hamiltonian can be written down from the above results and converted to numerical form for particular values of the quantum numbers. However, it is another matter to determine in advance which of these matrix elements vanish because of the symmetry of the molecule.

The choice of a suitable representation which will simplify diagonalization of the resultant matrices depends on the specific problem, and has been discussed for some examples by Bersohn (1949).

VII. Acknowledgments

The author would like to thank Mr. W. E. Smith for valuable criticism and suggestions.

VIII. References

Bardeen, J., and Townes, C. H. (1948*a*).—*Phys. Rev.* **73**: 97–105.
Bardeen, J., and Townes, C. H. (1948*b*).—*Phys. Rev.* **73**: 627–9, 1204.
Bersohn, R. (1949).—Ph.D. Thesis, Harvard University.
Bersohn, R. (1950).—*J. Chem. Phys.* **18**: 1124–5.
Bragg, J. K. (1948).—*Phys. Rev.* **74**: 533–8.
Condon, E. U., and Shortley, G. H. (1953).—"The Theory of Atomic Spectra." (Cambridge Univ. Press.)
Cross, P. C., Hainer, R. M., and King, G. W. (1944).—*J. Chem. Phys.* **12**: 210–43.
Foley, H. M. (1947).—*Phys. Rev.* **71**: 747–51.
Gordon, J. P. (1955).—*Phys. Rev.* **99**: 1253–63.
Gunther-Mohr, G. R., Townes, C. H., and Van Vleck, J. H. (1954).—*Phys. Rev.* **94**: 1191–203.
Güttinger, P., and Pauli, W. (1931).—*Z. Phys.* **67**: 743–65.
Hadley, G. F. (1955).—Ph.D. Thesis, Harvard University.
Herrmann, G. (1956).—New York University Rep. No. 289.6.
Myers, R. J., and Gwinn, W. D. (1952).—*J. Chem. Phys.* **20**: 1420–7.
Okaya, A. (1956).—*J. Phys. Soc. Japan* **11**: 249–58.
Racah, G. (1942).—*Phys. Rev.* **62**: 438–62.
Ramsey, N. F. (1956).—"Molecular Beams." (Clarendon Press: Oxford.)
Robinson, G. W., and Cornwell, C. D. (1953).—*J. Chem. Phys.* **21**: 1436–42.
Townes, C. H., and Schawlow, A. L. (1955).—"Microwave Spectroscopy." (McGraw-Hill: New York.)
Van Vleck, J. H. (1951).—*Rev. Mod. Phys.* **23**: 213–27.
White, R. L. (1955).—*Rev. Mod. Phys.* **27**: 276–88.