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EFFECTIVE HYPERFINE HAMILTONIAN IN HOMONUCLEAR DIATOMIC MOLECULES. APPLICATION TO THE B STATE OF MOLECULAR IODINE

M. BROYER, J. VIGUÉ and J. C. LEHMANN

Laboratoire de Spectroscopie Hertzienne de l'E.N.S. (*),
 24, rue Lhomond, 75231 Paris Cedex 05, France

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Résumé. — Le Hamiltonien hyperfin effectif est étudié pour les molécules diatomiques homonucléaires. A l'aide de l'algèbre des opérateurs tensoriels irréductibles, les termes de perturbation du second ordre dus aux Hamiltoniens dipolaires magnétiques et quadripolaires électriques sont calculés et le résultat est exprimé sous une forme concise. Ces calculs sont appliqués à l'état B de la molécule d'iode : les valeurs expérimentales des constantes du couplage spin-spin scalaire et tensorielle sont interprétées. De plus, on montre que la valeur de la constante de couplage octupolaire magnétique récemment publiée ne peut pas correspondre à la réalité et que des termes jusqu'ici négligés devraient être introduits dans le Hamiltonien hyperfin effectif.

Abstract. — The effective hyperfine Hamiltonian is studied in the case of homonuclear diatomic molecules, using irreducible tensorial algebra. The second order perturbation terms due to the magnetic dipole and electric quadrupole Hamiltonian are calculated in a compact form. These calculations are applied to the B state of molecular iodine : the experimental values of the scalar and tensorial spin-spin coupling constants are interpreted. Moreover it is shown that the recently published magnetic octupole coupling value for the B state is unrealistic and also that some other terms must be introduced in the hyperfine Hamiltonian.

1. Introduction. — With the recent development of narrow band lasers, it is possible to measure hyperfine structures in the excited states of diatomic molecules with great accuracy. As is well known, the hyperfine Hamiltonian of molecules violates the Born-Oppenheimer approximation. Therefore, it may couple different molecular electronic states. Such perturbations are generally much more important in excited states than in ground states since the density of electronic levels is much higher. The problem of the interpretation of the hyperfine structure in excited molecular states is therefore closely related to the problem of such perturbations. For example, in the $B^3\Pi_{0+}$ state of I_2 , many parameters which have been measured can be understood by a second order perturbation of the electronic molecular state : spin rotation constant, tensor spin-spin, scalar spin-spin, magnetic octupole, Landé factors, chemical shift, etc... However, up to now, no global theory of the effective hyperfine Hamiltonian has been made and

usually one simply selects in the literature the terms needed to fit the experimental results. In this paper a detailed derivation of the effective hyperfine Hamiltonian in a homonuclear diatomic molecule is presented. Our theory will be limited to second order of perturbation and the results will be applied to the B state of I_2 .

2. Hyperfine Hamiltonian. — The origin of the hyperfine molecular Hamiltonian lies in the interaction between the electric and magnetic multipoles of a nucleus with the electric and magnetic fields created by the electrons and the other nuclei. Due to parity conservation inside the nuclei, only the even electric ones and the odd magnetic multipoles are non vanishing. Moreover, the Wigner-Eckart theorem implies that the only existing 2^k -poles are those for which $k \leq 2 I_i$ where I_i is the spin of the considered nucleus.

Let us first consider the terms involving the interaction between the nuclei and the electrons. We will restrict ourselves to diatomic homonuclear molecules.

(*) Laboratoire associé au Centre National de la Recherche Scientifique.

2.1 INTERACTION BETWEEN ELECTRONS AND NUCLEI.

— This interaction can be written :

$$\mathcal{H}_{\text{hf}} = \mathcal{H}_{\text{hf}}(1) + \mathcal{H}_{\text{hf}}(2).$$

$\mathcal{H}_{\text{hf}}(1)$ is the hyperfine interaction between the electrons and nucleus labelled 1 ;

$\mathcal{H}_{\text{hf}}(2)$ the hyperfine interaction between the electrons and nucleus labelled 2.

Moreover, \mathcal{H}_{hf} contains all the multipole interactions :

$$\mathcal{H}_{\text{hf}} = \mathcal{H}_{\text{MD}} + \mathcal{H}_{\text{EQ}} + \mathcal{H}_{\text{MO}} + \mathcal{H}_{\text{EH}} + \dots$$

where

\mathcal{H}_{MD} is the magnetic dipole Hamiltonian

\mathcal{H}_{EQ} is the electric quadrupole Hamiltonian

\mathcal{H}_{MO} is the magnetic octupole Hamiltonian

\mathcal{H}_{EH} is the electric hexadecapole Hamiltonian

It is clear that $\mathcal{H}_{\text{MD}} = \mathcal{H}_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2)$, $\mathcal{H}_{\text{EQ}} = \mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2)$, etc...

$\alpha)$ *Magnetic dipole term.*

$$\mathcal{H}_{\text{MD}}(1) = \mathcal{H}_{\text{LI}}(1) + \mathcal{H}_{\text{SI}}(1) + \mathcal{H}_{\text{FI}}(1) :$$

• $\mathcal{H}_{\text{LI}}(1)$ is the interaction energy between the orbital electronic momentum and the magnetic moment of nucleus 1.

$$\mathcal{H}_{\text{LI}}(1) = \sum_e -2 g_{I_1} \mu_B \mu_N \left(\frac{\mu_0}{4\pi} \right) \frac{\mathbf{I}_1 \cdot \mathbf{l}_e(1)}{r_{1e}^3}.$$

The summation is over all electrons.

μ_B and μ_N are respectively the Bohr magneton and the nuclear magneton. μ_B is negative and μ_N positive.

We use the SI unit system $\left(\frac{\mu_0}{4\pi} = 10^{-7} \right)$. \mathbf{I}_1 and $\mathbf{l}_e(1)$ are dimensionless. $\mu_{I_1} = g_{I_1} \mu_N \mathbf{I}_1$, $\hbar \mathbf{l}_e(1) = \mathbf{r}_{1e} \wedge \mathbf{p}_e$, \mathbf{p}_e is the momentum of the electron e and $\mathbf{r}_{1e} = \mathbf{r}_e - \mathbf{r}_1$, \mathbf{r}_1 and \mathbf{r}_e being respectively the positions of nucleus 1 and electron e .

• $\mathcal{H}_{\text{SI}}(1)$ is the interaction energy between the spin of the nucleus 1 and the spins of the electrons

$$\mathcal{H}_{\text{SI}}(1) = \sum_e -g_S g_{I_1} \mu_B \mu_N \left(\frac{\mu_0}{4\pi} \right) \times \frac{3(\mathbf{S}_e \cdot \mathbf{r}_{1e})(\mathbf{I}_1 \cdot \mathbf{r}_{1e}) - (\mathbf{I}_1 \cdot \mathbf{S}_e)(\mathbf{r}_{1e} \cdot \mathbf{r}_{1e})}{r_{1e}^5}.$$

g_S is the Landé factor of the free electron. \mathbf{S}_e is the spin of electron e .

• $\mathcal{H}_{\text{FI}}(1)$ is the Fermi contact interaction energy :

$$\mathcal{H}_{\text{FI}}(1) = \sum_e -g_S g_{I_1} \mu_B \mu_N \left(\frac{\mu_0}{4\pi} \right) \frac{8\pi}{3} \mathbf{I}_1 \cdot \mathbf{S}_e \delta(\mathbf{r}_{1e}).$$

These three magnetic dipole terms have all the same tensorial form and by using the Wigner-Eckart theorem, $\mathcal{H}_{\text{MD}}(1)$ may be written :

$$\mathcal{H}_{\text{MD}}(1) = \sum_e \sum_q (-1)^q Q_q^1(\mathbf{I}_1) V_{-q}^1(\mathbf{j}_e(1))$$

where $\mathbf{j}_e(1) = \mathbf{l}_e(1) + \mathbf{S}_e$ and $Q_q^1(\mathbf{I}_1)$ and $V_{-q}^1(\mathbf{j}_e(1))$ are spherical tensor operators of rank 1.

$\beta)$ *Electric quadrupole term.*

$$\mathcal{H}_{\text{EQ}}(1) = \sum_e \sum_q (-1)^q Q_q^2(1) V_{-q}^2(1)$$

$$Q_q^2(1) = \sqrt{\frac{4\pi}{5}} \sum_{\substack{\text{protons } p \\ \text{of nucleus 1}}} e_p r_p^2 Y_q^2(\theta_p, \varphi_p)$$

r_p , θ_p and φ_p being the radial and angular coordinates of the protons p inside the nucleus.

$$V_{eq}^2(1) = \sqrt{\frac{4\pi}{5}} \frac{e}{4\pi\epsilon_0 r_{1e}^3} Y_q^2(\theta_{1e}, \varphi_{1e})$$

θ_{1e} , φ_{1e} being the angular coordinates of the vector \mathbf{r}_{1e} , and e the charge of the electron.

As for the case of $\mathcal{H}_{\text{MD}}(1)$, we may apply the Wigner-Eckart theorem and write $\mathcal{H}_{\text{EQ}}(1)$ as :

$$\mathcal{H}_{\text{EQ}}(1) = \sum_e \sum_q (-1)^q Q_q^2(\mathbf{I}_1) V_{-q}^2(\mathbf{j}_e(1))$$

$Q_q^2(\mathbf{I}_1)$ and $V_{-q}^2(\mathbf{j}_e(1))$ being spherical tensor operators of rank 2.

$\gamma)$ *Other multipole terms.* — We do not explicit in any detail \mathcal{H}_{MO} and \mathcal{H}_{EH} , but by application of the Wigner-Eckart theorem, they may be written :

$$\mathcal{H}_{\text{MO}}(1) = \sum_e \sum_q (-1)^q Q_q^3(\mathbf{I}_1) V_{-q}^3(\mathbf{j}_e(1))$$

$$\mathcal{H}_{\text{EH}}(1) = \sum_e \sum_q (-1)^q Q_q^4(\mathbf{I}_1) V_{-q}^4(\mathbf{j}_e(1))$$

$Q_q^k(\mathbf{I}_1)$ and $V_q^k(\mathbf{j}_e(1))$ are spherical tensor operators of rank k .

2.2 INTERACTION BETWEEN THE TWO NUCLEI. —

$\alpha)$ *Magnetic dipole term.* — The magnetic moment of one nucleus interacts with the orbital angular momentum of the other nucleus and both magnetic moments interact together.

$$\mathcal{H}_{\text{MD}}(1, 2) = \mathcal{H}_{\text{IR}}(1, 2) + \mathcal{H}_{\text{II}_2}(1, 2).$$

$\mathcal{H}_{\text{IR}}(1, 2)$ corresponds to the spin orbit and spin other orbit interactions between the two nuclei in motion. $\mathcal{H}_{\text{IR}}(1, 2)$ is equal [1] to :

$$\mathcal{H}_{\text{IR}}(1, 2) = 2(2g_I - 1) \frac{Z}{M_N} \frac{\mu_0}{4} \mu_N^2 \frac{(\mathbf{I}_1 + \mathbf{I}_2) \cdot \mathbf{R}}{r_{12}^3}.$$

Z is the charge of the nucleus, M_N its mass number,

$\frac{Z}{M_N} \left(\approx \frac{1}{2} \right)$ is dimensionless. \mathbf{R} is the angular momentum of the two nuclei. $\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}$ where \mathbf{J} is the total angular momentum of the molecule, \mathbf{L} the total orbital angular momentum of the electrons, and \mathbf{S} the total electronic spin. $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$

$$\mathcal{H}_{IR}(1, 2) = 2(2g_I - 1) \frac{\mu_0}{4\pi} \mu_N^2 \frac{\mathbf{I} \cdot (\mathbf{J} - \mathbf{L} - \mathbf{S})}{r_{12}^3}$$

where $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ is the total nuclear spin.

$\mathcal{H}_{I_1 I_2}(1, 2)$ is the direct spin-spin interaction between the two nuclei :

$$\mathcal{H}_{I_1 I_2} = -g_I^2 \mu_N^2 \frac{\mu_0}{4\pi} \times \frac{3(\mathbf{I}_1 \cdot \mathbf{r}_{12})(\mathbf{I}_2 \cdot \mathbf{r}_{12}) - (\mathbf{I}_1 \cdot \mathbf{I}_2)(\mathbf{r}_{12} \cdot \mathbf{r}_{12})}{r_{12}^5}$$

β) *Electric quadrupole term.* — The quadrupole of one nucleus interacts with the gradient of the electric field created by the charge of the other

$$\mathcal{H}_{EQ}(1, 2) = \sum_q (-1)^q Q_q^2(1) V_{-q}^2(1, 2) + (-1)^q Q_q^2(2) V_{-q}^2(2, 1)$$

$Q_q^2(1)$ and $Q_q^2(2)$ have been already defined.

$$V_q^2(1, 2) = \sqrt{\frac{4\pi}{5}} \frac{(-Ze)}{4\pi\epsilon_0 r_{12}^3} Y_q^2(\theta_{12}, \varphi_{12})$$

r_{12} , θ_{12} , φ_{12} are the spherical coordinates of the vector \mathbf{r}_{12} . We have evidently

$$Y_q^2(\theta_{12}, \varphi_{12}) = Y_q^2(\theta_{21}, \varphi_{21})$$

We must also take into account the interaction between the two electric quadrupoles of the two nuclei $\mathcal{H}_{Q_1 Q_2}(1, 2)$. This term is very similar to the magnetic dipole-dipole term $\mathcal{H}_{I_1 I_2}$ and is proportional to

$$\sum_q (-1)^q (Q^2(\mathbf{I}_1) \cdot Q^2(\mathbf{I}_2))_q^4 \cdot V_{-q}^4(1, 2)$$

Similarly we have also the interaction $\mathcal{H}_{OM}(1, 2)$ between the octupole of one nucleus and the magnetic dipole of the other or the magnetic dipole due to the rotation of the molecule, etc...

As we will see in the next paragraph (Table I), these last terms are negligible.

γ) *Order of magnitude of the hyperfine terms.* — We express here the various terms as a function of the mass energy of the electron mc^2 , the fine structure constant α , the charge number Z , the electron to proton mass ratio m/M .

r_N is the radius of a nucleus, r_{1e} the distance between a nucleus and the electron e , r_{12} the distance between the nuclei. a_0 is the Bohr radius.

Some dimensionless factors of the order of unity are neglected. The electric 2^k -pole is taken equal to er_N^k ; the magnetic 2^k -pole to $\mu_N r_N^{k-1}$.

The results are given in table I.

The third column gives numerical evaluation of these terms in the case of iodine ($Z = 53$). The atomic fine structure is used to evaluate $\langle a_0^3/r_{1e}^3 \rangle$ (the order of magnitude being the same for molecular wave functions); the atomic magnetic octupole is used to evaluate $\langle a_0^5/r_{1e}^5 \rangle$. r_N^2 is taken from Schwartz [17]

$$\left\langle \frac{a_0^3}{r_{1e}^3} \right\rangle = 13 \quad \left\langle \frac{a_0^5}{r_{1e}^5} \right\rangle = 570 \quad \frac{r_N^2}{a_0^2} = 1.8 \times 10^{-8}$$

r_{12} is taken from molecular results [5] $r_{12} \approx 3 \text{ \AA}$.

The shielding effects due to the core electrons have not been taken into account. These effects will reduce the direct interactions terms between the two nuclei.

The fourth column contains the values of the parameters observed in the ground state of atomic iodine.

The simplifying assumptions that we have made for our estimations imply that the results can be wrong by a fraction of one order of magnitude. Evidently the selection rules have not been taken into account : for instance the $\mathbf{I} \cdot \mathbf{L}$ term of the hyperfine structure that we find of the order of $2 \times 10^9 \text{ Hz}$ will be zero in an $\Omega = 0$ state (as noted below).

2.3 CONCLUSION. — As a conclusion of this paragraph 2, we can write the hyperfine Hamiltonian as :

$$\mathcal{H}_{\text{hf}} = \mathcal{H}_{\text{hf}}(1) + \mathcal{H}_{\text{hf}}(2) + \mathcal{H}_{\text{hf}}(1, 2)$$

$\mathcal{H}_{\text{hf}}(1)$ involves the interaction between the electrons and the nucleus 1, $\mathcal{H}_{\text{hf}}(2)$ the interaction between the electrons and the nucleus 2, $\mathcal{H}_{\text{hf}}(1, 2)$ is the direct interaction between the two nuclei.

Moreover, we have shown that order of magnitude of the various terms can be easily given.

3. Matrix elements of the different terms of \mathcal{H}_{hf} .

For all calculations which are presented in this paper, we use as a basis set of vectors $|S; A, \Sigma, \Omega, v; J; (I_1 I_2) I; F; M_F\rangle$ where $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ and $\mathbf{F} = \mathbf{I} + \mathbf{J}$. A, S, Σ, Ω are the usual molecular quantum numbers. This means that we use a Hund's case a representation but our results are easily generalizable to a case c representation. v is the vibrational quantum number or eventually it is a continuous index for a continuum of dissociation.

3.1 SYMMETRY PROPERTIES OF THE MATRIX ELEMENTS.

— Since the molecules under consideration are homonuclear, the rotational levels are ortho or para and therefore the I values are restricted :

For example for $I_1 = I_2 = 3/2$ the ortho states

TABLE I
Order of magnitude of the hyperfine terms

Hamiltonian	Energy/mc ²	Energy/h (Hz) estimated for atomic and molecular iodine	Energy/h (Hz) measured in the ² P _{3/2} of the ¹²⁷ I atom
Fine structure	$\alpha^4 Z \left\langle \frac{a_0^3}{r_{1e}^3} \right\rangle$	(^a)	2×10^{14}
Hyperfine structure			
1) <i>Magnetic dipole</i>			
I.L or I.S	$\alpha^4 \frac{m}{M} \left\langle \frac{a_0^3}{r_{1e}^3} \right\rangle$	2×10^9	8×10^8 (^c)
I₁.I₂	$\alpha^4 \left(\frac{m}{M} \right)^2 \left\langle \frac{a_0^3}{r_{12}^3} \right\rangle$	5×10^2	
I₁.R	$\alpha^4 \left(\frac{m}{M} \right)^2 \left\langle \frac{a_0^3}{r_{12}^3} \right\rangle J$	5×10^2 J	
2) <i>Electric quadrupole</i>			
Nucleus-electron $\mathcal{H}_{EQ}(1) + \mathcal{H}_{EQ}(2)$	$\alpha^2 \frac{r_N^2}{a_0^2} \left\langle \frac{a_0^3}{r^3} \right\rangle$	10^9	10^9 (^c)
Nucleus-Nucleus :			
Quadrupole-charge $\mathcal{H}_{EQ}(1, 2)$	$\alpha^2 \frac{r_N^2}{a_0^2} \left\langle \frac{a_0^3}{r_{12}^3} \right\rangle Z$	3×10^7	
Quadrupole-quadrupole $\mathcal{H}_{Q_1Q_2}(1, 2)$	$\alpha^2 \frac{r_N^4}{a_0^4} \left\langle \frac{a_0^5}{r_{12}^5} \right\rangle$	3×10^{-4} (negligible)	
3) <i>Magnetic octupole</i>			
Nucleus-electron $\mathcal{H}_{OM}(1) + \mathcal{H}_{OM}(2)$	$\alpha^4 \frac{m}{M} \frac{r_N^2}{a_0^2} \left\langle \frac{a_0^5}{r^5} \right\rangle$	(^b)	2×10^3 (^c)
Nucleus-nucleus $\mathcal{H}_{OM}(1, 2)$	$\alpha^4 \left(\frac{m}{M} \right)^2 \frac{r_N^2}{a_0^2} \left\langle \frac{a_0^5}{r_{12}^5} \right\rangle J$	10^{-6} J (negligible)	
4) <i>Electric hexadecapole</i>			
Nucleus-electron $\mathcal{H}_{EH}(1) + \mathcal{H}_{EH}(2)$	$\alpha^2 \frac{r_N^4}{a_0^4} \left\langle \frac{a_0^5}{r_{1e}^5} \right\rangle$	10^3	
Nucleus-nucleus $\mathcal{H}_{EH}(1, 2)$	$\alpha^2 \frac{r_N^4}{a_0^4} \left\langle \frac{a_0^5}{r_{1e}^5} \right\rangle Z$	10^{-2} (negligible)	

(^a) The measured atomic fine structure is used to estimate $\langle 1/r_{1e}^3 \rangle$.

(^b) The measured octupole constant is used to estimate $\langle 1/r_{1e}^5 \rangle$.

(^c) Taken from reference [11].

correspond to $I = 1$ and 3, and the para states to $I = 0$ and 2. For $I_1 = I_2 = 5/2$ (as for ¹²⁷I), ortho states correspond to $I = 1, 3, 5$, para states to $I = 0, 2, 4$.

The unperturbed electronic wave functions of homonuclear molecules are even (g) or odd (u) with respect to the centre of the molecule. However, the hyperfine Hamiltonian is not invariant by reflexion of the electrons with respect to the center of the

molecule, therefore it can couple u and g electronic states.

By using only symmetry considerations one can show [2] that :

$$\begin{aligned}
 \langle uI' | \mathcal{H}_{hf}(1) | uI \rangle &= (-1)^{I+I'} \langle uI' | \mathcal{H}_{hf}(2) | uI \rangle \\
 \text{and} \\
 \langle uI' | \mathcal{H}_{hf}(1) | gI \rangle &= (-1)^{I+I'+1} \langle uI' | \mathcal{H}_{hf}(2) | gI \rangle.
 \end{aligned}
 \tag{1}$$

Since it does not involve the electrons, $\mathcal{H}_{\text{hf}}(1, 2)$ does not have the same symmetry properties :

$$\langle uI' | \mathcal{H}_{\text{hf}}(1, 2) | uI \rangle = (-1)^{I+I'} \langle uI' | \mathcal{H}_{\text{hf}}(1, 2) | uI \rangle$$

but

$$\langle uI' | \mathcal{H}_{\text{hf}}(1, 2) | gI \rangle = 0.$$

It is easy to see that these relations ensure that \mathcal{H}_{hf} does not violate the Pauli principle of symmetry and antisymmetry of the total eigenfunction by exchange of the two identical nuclei. For example ortho and para rotational levels of two u states cannot be coupled by \mathcal{H}_{hf} . But the ortho rotational levels of a g state can be coupled with the para levels of a u state. As already pointed out by Herzberg [3], the ortho or para character is no longer absolutely meaningful in presence of a hyperfine structure.

3.2 CALCULATION OF THE DIFFERENT MATRIX ELEMENTS. — We want now to obtain the matrix elements of \mathcal{H}_{hf} between two electronic states which may or

may not be different, in order to perform a second order perturbation calculation. This type of calculation has been already made by Freed [4] in the case of heteronuclear molecules when only one of the nuclei has a nuclear spin. Freed's results are evidently valid for a homonuclear molecule if we use the basis set $|SA\Sigma\Omega v, JI_1 F_1 M_{F_1} I_2 M_{I_2}\rangle$ for $\mathcal{H}_{\text{hf}}(1)$. ($F_1 = J + I_1$). To obtain the matrix elements of $\mathcal{H}_{\text{hf}}(1)$ in the good basis set $|SA\Sigma\Omega v J(I_1 I_2) IFM_F\rangle$ one has to use the usual angular-momentum algebra. The results are the following. They are derived for a neutral homonuclear molecule in which A, S, Σ, Ω and J, I, F are integer.

$\alpha)$ *Matrix elements of $\mathcal{H}_{\text{hf}}(1)$.* — $\mathcal{H}_{\text{hf}}(1)$ may be written :

$$\mathcal{H}_{\text{hf}}(1) = \sum_k \mathcal{H}^k(1)$$

where $\mathcal{H}^k(1)$ is a tensorial interaction of rank k between the nucleus 1 and the electrons (see paragraph 2)

$$\begin{aligned} \langle S' A' \Omega' v' J'(I_1 I_2) I' F' M_F' | \mathcal{H}^k(1) | SA\Sigma\Omega v J(I_1 I_2) IFM_F \rangle = \\ = \delta_{FF'} \delta_{M_F M_F'} (-1)^{k+I_1+I_2+F+I'+J+J'} f_k(1, \Omega', \Omega) [(2I+1)(2I'+1)(2J+1)(2J'+1)]^{1/2} \\ \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{Bmatrix} I_2 & I_1 & I \\ k & I' & I_1 \end{Bmatrix} \begin{Bmatrix} F & I' & J' \\ k & J & I \end{Bmatrix} \end{aligned} \quad (3)$$

$$\Delta\Omega = \Omega' - \Omega.$$

$f_k(1, \Omega', \Omega)$ depends also upon S', A', S, A, v, v' , etc... This dependence is here suppressed in order to simplify the notation. In fact $f_k(1, \Omega', \Omega)$ contains the electronic reduced matrix elements of the hyperfine interaction of rank k and also a Franck-Condon integral. If the electronic reduced matrix elements are almost independent of r_{12} , the internuclear distance, $f_k(1, \Omega', \Omega)$, is proportional to the Franck-Condon integral $\langle v' | v \rangle$ to a good approximation. The detailed expressions of $f_1(1, \Omega, \Omega')$ and $f_2(1, \Omega, \Omega')$ are given in table II.

Expression (3) is very similar to the formula which should be obtained for a 2^k -poles hyperfine interaction in an atom. However, the 3j symbol $\begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix}$ and the 6j symbol $\begin{Bmatrix} I_2 & I_1 & I \\ k & I' & I_1 \end{Bmatrix}$ do not appear in the corresponding formula in the case of atoms. The 6j symbol $\begin{Bmatrix} I_2 & I_1 & I \\ k & I' & I_1 \end{Bmatrix}$ corresponds to the coupling of the two nuclear spins I_1 and I_2 . The 3j symbol $\begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix}$ appears when a tensorial operator of rank k has to be averaged over the molecular rotation. This is the case of the magnetic and electric

fields (or their derivatives) created by the electrons at the position of the given nucleus.

If we consider a molecule in a given electronic state ($\Omega' = \Omega$), every *electronic* physical operator (for example the magnetic field created by the electrons) must at first be averaged over the electronic motion, the nuclei being assumed to be at rest, and then averaged over the nuclear motion (vibration and rotation). As a result of the averaging over the electronic motion and of the cylindrical symmetry around the internuclear axis, only the longitudinal part of the various electronic operators does not vanish. For instance, the only non-zero component of the magnetic field created by the electrons is along the internuclear axis. The averaging over the vibration is straight forward. The averaging over the molecular rotation introduces the 3j symbol of formula (3).

The existence of this 3j symbol has an important consequence: Since $\begin{pmatrix} J & k & J \\ 0 & 0 & 0 \end{pmatrix} = 0$ for odd values of k , the 2^k -polar interactions vanish for odd values of k in a molecular state $\Omega = 0$. This property may be illustrated by the following classical and rather naive argument. If $\Omega = 0, J$ the total angular momentum of the molecule (nuclear spin excluded) is perpendicular to the internuclear axis, and the rotation axis of the molecule is therefore perpendicular to the

TABLE II

Expression of $f_1(1, \Omega', \Omega)$ and of $f_2(1, \Omega', \Omega)$

In fact $f_1(1, \Omega', \Omega) = f_1(1, S', A', \Sigma', \Omega', v', S, A, \Sigma, \Omega, v)$

$f_2(1, \Omega', \Omega) = f_2(1, S', A', \Sigma', \Omega', v', S, A, \Sigma, \Omega, v)$

$$f_1(1, S', A', \Sigma', \Omega', v, S, A, \Sigma, \Omega, v) = \left[(-1)^{-A+1+S'} \begin{pmatrix} S' & 1 & S \\ \Sigma' & -\Delta\Sigma & -\Sigma \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ \Delta\Sigma & -\Delta\Sigma & -\Delta A \end{pmatrix} \times \right. \\ \left. \times D_{A'A}^{S'S}(1) + \delta_{\Sigma'\Sigma} \delta_{S'S} (-1)^{-\Omega'} G_{A'A}(1) + (-1)^{-A+1+S'-\Sigma'+\Sigma} \right. \\ \left. \times \begin{pmatrix} S' & 1 & S \\ \Sigma' & -\Delta\Sigma & -\Sigma \end{pmatrix} K_{A'A}^{S'S}(1) \right] [I_1(I_1+1)(2I_1+1)]^{1/2} \\ \Delta\Sigma = \Sigma' - \Sigma \quad \Delta A = A' - A.$$

$D_{A'A}^{S'S}(1)$ is the reduced matrix element of $\mathcal{H}_{SI}(1)$:

$$D_{A'A}^{S'S}(1) = -g_S g_{I_1} \mu_B \mu_N \frac{\mu_0}{4\pi} \left\langle S' A' v' \left\| \sum_e \sqrt{\frac{4\pi}{5}} T^1(\mathbf{S}_e) \frac{Y_{\Delta A}^2(\theta_{1e}, \varphi_{1e})}{r_{1e}^3} \right\| S A v \right\rangle.$$

$G_{A'A}(1)$ is the reduced matrix element of $\mathcal{H}_{LI}(1)$:

$$G_{A'A}(1) = -2 g_{I_1} \mu_B \mu_N \frac{\mu_0}{4\pi} \left\langle A' v' \left\| \sum_e \frac{T_{\Delta A}^1(\mathbf{l}_e)}{r_{1e}^3} \right\| A v \right\rangle.$$

$K_{A'A}^{S'S}(1)$ is the reduced matrix element of $\mathcal{H}_{FI}(1)$:

$$K_{A'A}^{S'S}(1) = -\frac{8\pi}{3} g_S g_{I_1} \mu_B \mu_N \frac{\mu_0}{4\pi} \delta_{A'A} \left\langle S' A' v' \left\| \sum_e T^1(\mathbf{S}_e) \delta(\mathbf{r}_{1e}) \right\| S A v \right\rangle$$

(μ_B is negative)

$$f_2(1, S', A', \Sigma', \Omega', v', S, A, \Sigma, \Omega, v) = (-1)^{\Omega'} Q_{A'A}(1) [(2I_1+3)(2I_1+2)(2I_1+1)/2 I_1(2I_1-1)]^{1/2}$$

$$Q_{A'A}(1) = \frac{1}{4} |e| Q(1) q_{A'A}(1)$$

$$Q(1) = \left\langle I_1 M_{I_1} = I_1 \left| \sum_{\substack{\text{protons of} \\ \text{nucleus 1}}} (3z_p^2 - r_p^2) \right| I_1 M_{I_1} = I_1 \right\rangle = Q$$

$$\frac{1}{2} q_{A'A}(1) = \left\langle A' \left\| \sum_e \frac{e}{4\pi\epsilon_0 r_{1e}^3} \sqrt{\frac{4\pi}{5}} Y_{\Delta A}^2(\theta_{1e}, \varphi_{1e}) \right\| A \right\rangle.$$

If $|A'\rangle = |A\rangle$, $q_{AA} = q$ and $|e| Q(1) q_{AA}(1)$ is usually noted eqQ .

internuclear axis. Under these conditions, if the longitudinal part of an electronic operator changes sign when the molecule is rotated by 180°, the averaged value of this operator will be zero. For instance, this is the case for the magnetic field created by one electron along the internuclear axis. However, this is not the

case for the gradient of the electric field created by one electron at the nuclei.

In conclusion, in molecular states $\Omega = 0$, the hyperfine interaction of rank k vanishes to first order for odd values of k . For such states, the second order hyperfine terms are particularly important.

β) Matrix elements of $\mathcal{H}_{\text{hf}}(1, 2)$

$$\mathcal{H}_{IR}(1, 2) = (4g_I - 2) \mu_N^2 \frac{\mu_0}{4\pi} \frac{Z}{M_N} \left(\frac{\mathbf{I} \cdot \mathbf{J}}{r_{12}^3} - \frac{\mathbf{I} \cdot (\mathbf{L} + \mathbf{S})}{r_{12}^3} \right).$$

The first part of \mathcal{H}_{IR} cannot couple different electronic states

$$\left\langle \Omega' v' J' I' F \left| \frac{\mathbf{I} \cdot \mathbf{J}}{r_{12}^3} \right| \Omega v J I F \right\rangle = \delta_{\Omega' \Omega} \delta_{J' J} \delta_{I' I} \left\langle \Omega v' \left| \frac{1}{r_{12}^3} \right| \Omega v \right\rangle \frac{1}{2} [F(F+1) - I(I+1) - J(J+1)]. \quad (4)$$

The second part is very similar to $\mathcal{H}_{LI}(1)$. But it does not couple u and g states and it is diagonal in I :

$$\begin{aligned} \left\langle \Omega' v' J' I' F \left| \frac{\mathbf{I} \cdot (\mathbf{L} + \mathbf{S})}{r_{12}^3} \right| \Omega v J I F \right\rangle &= \delta_{I' I} (-1)^{\Omega'} \begin{pmatrix} J' & 1 & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \times \\ &\times [(2J'+1)(2J+1)I(I+1)(2I+1)]^{1/2} (-1)^{I+F+J'+J} \begin{Bmatrix} F & I & J' \\ 1 & J & I \end{Bmatrix} \left\langle \Omega' v' \left| \frac{T_{\Delta\Omega}^1(\mathbf{L}) + T_{\Delta\Omega}^1(\mathbf{S})}{r_{12}^3} \right| \Omega v \right\rangle. \end{aligned} \quad (5)$$

This last term is $\mu_B/\mu_N \sim 2000$ times smaller than $\mathcal{H}_{LI}(1)$ and can be neglected in a second order perturbation calculation.

$\mathcal{H}_{I_1 I_2}(1, 2)$ is diagonal for the electronic eigenfunctions because it contains only the coordinates of the nuclei (\mathbf{r}_{12}). The matrix elements of $\mathcal{H}_{I_1 I_2}$ have been derived by Bunker [5] :

$$\begin{aligned} \langle \Omega' v' J' I' F | \mathcal{H}_{I_1 I_2} | \Omega v J I F \rangle &= \delta_{\Omega' \Omega} g_I^2 \mu_N^2 \left\langle v' \left| \frac{1}{r_{12}^3} \right| v \right\rangle \frac{\mu_0}{4\pi} \times \\ &\times I_1(I_1+1)(2I_1+1)(-1)^{I'+F+1+J+J'} (30(2I+1)(2I'+1))^{1/2} ((2J+1)(2J'+1))^{1/2} \\ &\times \begin{pmatrix} J' & 2 & J \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{Bmatrix} F & J & I \\ 2 & I' & J' \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I' & 2 \end{Bmatrix} \end{aligned} \quad (6)$$

(there is a misprint in the 6j in Bunker's formula).

In the same way $\mathcal{H}_{EQ}(1, 2)$ is also diagonal for the electronic eigenfunctions because it contains only the coordinates of the nuclei. The matrix elements of $\mathcal{H}_{EQ}(1, 2)$ are easily derivable using the known matrix elements of the spherical harmonics in the rotational eigenfunctions basis (see for instance Ref. [6]) :

$$\begin{aligned} \langle \Omega' v' J' I' F | \mathcal{H}_{EQ}(1, 2) | \Omega v J I F \rangle &= \delta_{\Omega' \Omega} 2 \times (-1)^{\Omega+2+I_1+I_2+F+I'} \times \\ &\times \left[\frac{(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} \right]^{1/2} [(2I+1)(2I'+1)(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J' & 2 & J \\ -\Omega & 0 & \Omega \end{pmatrix} \\ &\times \begin{Bmatrix} 2 & I_1 & I_1 \\ I_1 & I' & I \end{Bmatrix} \begin{Bmatrix} F & J & I \\ 2 & I' & J' \end{Bmatrix} \frac{(-Ze)Q}{2} \left\langle \Omega v' \left| \frac{1}{4\pi\epsilon_0 r_{12}^3} \right| \Omega v \right\rangle \end{aligned} \quad (7)$$

where

$$Q = \left\langle I_1 M_{I_1} = I_1 \left| \sum_p (3z_p^2 - r_p^2) \right| I_1 M_{I_1} = I_1 \right\rangle.$$

It must be remarked that inside a given electronic state Ω , $\mathcal{H}_{EQ}(1, 2)$ has exactly the same dependence on $I' I, J', J, F$ as $\mathcal{H}^2(1)$ (see formula (3)). We would have similar considerations for $\mathcal{H}_{MO}(1, 2)$, $\mathcal{H}_{Q_1 Q_2}$, $\mathcal{H}_{EH}(1, 2)$. In conclusion, $\mathcal{H}_{hf}(1, 2)$ is essentially diagonal with respect to the electronic wave functions and its off diagonal part may be neglected. Therefore we will drop it in our second-order perturbation calculation and discuss its influence at the end of the paper.

4. Second order perturbation theory. — As already noted, it is especially important to consider second-order perturbation theory when $\Omega = 0$ since in this case the only important diagonal term is due to

$\mathcal{H}_{EQ}(k=2)$. However, we derive the theory for any value of Ω .

The perturbing Hamiltonian can be written :

$$\begin{aligned} \mathcal{H}_p &= \mathcal{V} + \mathcal{H}_{hf}(1) + \mathcal{H}_{hf}(2) + \mathcal{H}_{hf}(1, 2) \\ &= \mathcal{V} + \mathcal{H}_{hf}(1, 2) + \sum_k \mathcal{H}^k(1) + \mathcal{H}^k(2) \end{aligned}$$

where \mathcal{V} is the off-diagonal term of the molecular Hamiltonian which does not contain the nuclear spin I . \mathcal{V} contains mainly the fine structure Hamiltonian and the off diagonal part of the rotational Hamiltonian $\left(-\frac{\hbar^2}{\mu r_{12}^2} \mathbf{J}(\mathbf{L} + \mathbf{S}) \right)$.

If the fine structure Hamiltonian is too large, the appropriate basis set is a case c one in which the fine structure Hamiltonian is already diagonalized. In fact, we will write now the molecular eigenstates $|\Omega v J I F\rangle$. In these conditions, the results will be available for the Hund case a and the Hund case c, the difference between the two coupling cases appear-

ing only in the calculation of the electronic reduced matrix elements.

Up to second order effects, the matrix elements of the effective hyperfine Hamiltonian in a given rotational vibrational level of a diatomic homonuclear molecule are therefore given by :

$$\begin{aligned} \langle \Omega v J I'' F | \mathcal{H}_{\text{hf effective}} | \Omega v J I F \rangle = & \left\langle \Omega v J I'' F \left| \mathcal{H}_{\text{hf}}(1, 2) + \sum_k \mathcal{H}^k(1) + \mathcal{H}^k(2) \right| \Omega v J I F \right\rangle + \\ & + \sum_p \frac{\left\langle \Omega v J I'' F \left| \mathcal{V} + \sum_k \mathcal{H}^k(1) + \mathcal{H}^k(2) \right| p \right\rangle \left\langle p \left| \mathcal{V} + \sum_k \mathcal{H}^k(1) + \mathcal{H}^k(2) \right| \Omega v J I F \right\rangle}{E_{\Omega v J} - E_p} \end{aligned} \quad (8)$$

where $|p\rangle$ is a perturbing level of energy E_p .

As has been already noted, $\mathcal{H}_{\text{hf}}(1, 2)$ is not considered at second order since it is essentially diagonal for the electronic eigenfunctions.

We shall assume in our calculations that

$$|E_{\Omega v J} - E_p| \gg \Delta E_{\text{hf}},$$

ΔE_{hf} being the total hyperfine structure. In the case of an accidental coincidence between two interacting hyperfine structures, the situation would have to be studied by an exact diagonalization of the total Hamiltonian.

The perturbing levels $|p\rangle$ may be the ro-vibrational levels belonging not only to other electronic states but also to the state under consideration. $|p\rangle$ may be written $|\Omega' v' J' I' F\rangle$ and $E_p = E_{\Omega' v' J'}$.

The second order term involving \mathcal{V} twice is of no interest in our problem since it takes the same value for all the hyperfine sublevels. Let us consider now the other second order terms.

4.1 THE CROSS TERMS $\mathcal{V} - \mathcal{H}^k(i)$ ($i = 1, 2$). — \mathcal{V} operates only between states for which $\Delta I = 0$

and $\Delta J = 0$ and it accounts only for the coupling between two different electronic states. Since the matrix elements of \mathcal{V} do not depend on I and F , the second order terms of this type have the same I and F dependence as the diagonal matrix elements of $\mathcal{H}^k(i)$. However they may be sometimes identified, for instance when the diagonal matrix element of $\mathcal{H}^k(i)$ vanishes. Moreover systematic measurements of the hyperfine splittings as a function of v and J may also give some evidence of the existence of such terms : the perturbation may vary with v and J . For instance, if \mathcal{V} is the off-diagonal part of the rotational Hamiltonian, it must be linear in J .

4.2 THE CROSS TERMS

$$\mathcal{H}^k(i) - \mathcal{H}^{k'}(j) \quad (i = 1, 2; j = 1, 2).$$

The calculation of these terms are tedious and are detailed in appendix I. We give here only an outline of this calculation and some explanations giving the physical insight of this problem.

We have to consider the following terms :

$$\sum_{\Omega' v'} \sum_{J' I'} \frac{\langle \Omega v J I'' F | \mathcal{H}^k(i) | \Omega' v' J' I' F \rangle \langle \Omega' v' J' I' F | \mathcal{H}^{k'}(j) | \Omega v J I F \rangle}{E_{\Omega v J} - E_{\Omega' v' J'}}. \quad (9)$$

Let us note :

$$\mathcal{H}^{kk'}(i, j) = \sum_{\Omega' v'} \sum_{J' M'_J I' M'_I} \frac{\mathcal{H}^k(i) | \Omega' v' J' M'_J I' M'_I \rangle \langle \Omega' v' J' M'_J I' M'_I | \mathcal{H}^{k'}(j)}{E_{\Omega v J} - E_{\Omega' v' J'}}. \quad (10)$$

The summations on I' and J' are the summations on the hyperfine structure and on the rotation of the molecule. As we will see, it is generally possible to carry out these two summations and this is sufficient to obtain the angular properties of $\mathcal{H}^{kk'}(i, j)$. Therefore, in the following part of this paragraph, we will

consider that Ω' and v' have fixed values and omit temporarily the summations over Ω' and v' .

As we have seen in paragraph 2.1 $\mathcal{H}^k(i)$ may be written :

$$\sum_e \sum_q (-1)^q \mathcal{Q}_{-q}^k(\mathbf{I}_i) V_q^k(\mathbf{j}_e(i)).$$

However, if we limit ourselves to the matrix elements of $\mathcal{H}^k(i)$ between two given electronic states $|\Omega\rangle$ and $|\Omega'\rangle$, the Wigner-Eckart theorem insures that $\mathcal{H}^k(i)$ may be written :

$$\mathcal{H}^k(i) = g(\Omega, \Omega') \sum_q (-1)^q Q_{-q}^k(\mathbf{I}_i) V_q^k(\mathbf{J}_e) \quad (11)$$

where \mathbf{J}_e is the total electronic angular momentum of the molecule, and $V_q^k(\mathbf{J}_e)$ an irreducible tensor operator acting on \mathbf{J}_e . $Q_{-q}^k(\mathbf{I}_i)$ is an irreducible tensor operator acting on the nuclear spin \mathbf{I}_i of nucleus i . $g(\Omega, \Omega')$ depends upon the considered states $|\Omega\rangle$ and $|\Omega'\rangle$.

If it is now assumed that the energy difference between the neighbouring rotational levels is much smaller than the energy difference between states $|\Omega\rangle$ and $|\Omega'\rangle$, the energy denominator which appears in formulae (9) and (10) can be factorized and the summations on I' and J' easily made. In the course of these summations, we use the closure rules :

$$\sum_{I' M' I} |I' M' I\rangle \langle I' M' I| = 1$$

$$\sum_{J' M' J} |J' M' J\rangle \langle J' M' J| = |\Omega'\rangle \langle \Omega'|.$$

Under these conditions, a cross term $\mathcal{H}^{kk'}(i, j)$ is equal to :

$$\sum_{\Omega' v'} \frac{g(\Omega, \Omega') g(\Omega', \Omega)}{E_{\Omega v J} - E_{\Omega' v' J}} \times \sum_{qq'} (-1)^{q+q'} Q_{-q}^k(\mathbf{I}_i) Q_{-q'}^{k'}(\mathbf{I}_j) V_q^k(\mathbf{J}_e) V_{q'}^{k'}(\mathbf{J}_e). \quad (12)$$

Now we can take advantage of the usual rules of the decomposition of the various tensor operators $Q_{-q}^k(\mathbf{I}_i) Q_{-q'}^{k'}(\mathbf{I}_j)$ (or $V_q^k(\mathbf{J}_e) V_{q'}^{k'}(\mathbf{J}_e)$) on an irreducible tensorial basis set. In the course of this decomposition, terms of the following type arise :

$$\sum_Q (-1)^Q (Q^k(\mathbf{I}_i) \otimes Q^{k'}(\mathbf{I}_j))_{-Q}^K (V^k(\mathbf{J}_e) \otimes V^{k'}(\mathbf{J}_e))_Q^K \quad (13)$$

$(Q^k(\mathbf{I}_i) \otimes Q^{k'}(\mathbf{I}_j))_{-Q}^K$ is an irreducible tensorial operator of rank K constructed from the tensorial contract

product of $Q^k(\mathbf{I}_i)$ and $Q^{k'}(\mathbf{I}_j)$. The same notation is used for the operators $V^k(\mathbf{J}_e)$ and $V^{k'}(\mathbf{J}_e)$.

All tensorial orders K in agreement with the triangle rule $|k - k'| \leq K \leq |k + k'|$ appear in $\mathcal{H}^{kk'}(i, j)$.

At this point, we must distinguish two types of terms :

$\alpha) i = j$ - terms $\mathcal{H}^{kk'}(i, i)$. — The tensorial operators $(Q^k(\mathbf{I}_i) \otimes Q^{k'}(\mathbf{I}_i))_{-Q}^K$ are all equivalent for any values of k and k' and they are proportional to $Q_{-Q}^K(\mathbf{I}_i)$. This is just the Wigner-Eckart theorem. In the same way, the tensorial operators

$$(V^k(\mathbf{J}_e) \otimes V^{k'}(\mathbf{J}_e))_Q^K$$

are all equivalent and proportional to $V_Q^K(\mathbf{J}_e)$. Therefore formula (13) becomes :

$$\sum_Q (-1)^Q Q_{-Q}^K(\mathbf{I}_i) V_Q^K(\mathbf{J}_e). \quad (14)$$

We obtain an important result : *the second order terms involving the same nucleus twice have the same angular dependence as the first order term*. Physically this is easy to understand : in the present case, even at second order, we have always an interaction between the nucleus i and the electronic cloud. Such an interaction can be decomposed in scalar products of different tensorial orders.

$\beta) i \neq j$ - terms $\mathcal{H}^{kk'}(i, j)$. — $\mathcal{H}^{kk'}(i, j)$ is then proportional to

$$\sum_Q (-1)^Q (Q^k(\mathbf{I}_i) \otimes Q^{k'}(\mathbf{I}_j))_{-Q}^K V_Q^K(\mathbf{J}_e). \quad (14')$$

The tensorial operators $(Q^k(\mathbf{I}_i) \otimes Q^{k'}(\mathbf{I}_j))_{-Q}^K$ with $i \neq j$ are different operators for each set of k and k' values. *These terms will give angular dependences in the effective hyperfine Hamiltonian which do not exist at first order*. This is easy to physically interpret : a cross term $\mathcal{H}^k(i) \mathcal{H}^{k'}(j)$ creates, at second order, an interaction between nucleus i and nucleus j through the electronic cloud. The interaction evidently depends on k and k' .

The result of the exact calculation performed in appendix I is the following :

$$\begin{aligned} \langle \Omega v J I'' F | \mathcal{H}^{kk'}(i, j) | \Omega v J I F \rangle = & \sum_{\Omega' v'} \frac{(-1)^{\Omega' + k + k'}}{E_{\Omega v J} - E_{\Omega' v' J'}} f_k^*(1, \Omega', \Omega) f_{k'}(1, \Omega', \Omega) \sum_K (2K + 1) \times \\ & \times \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{Bmatrix} I_1 & K & I_1 \\ k' & I_1 & k \end{Bmatrix} (-1)^F (2J + 1) [(2I'' + 1)(2I + 1)]^{1/2} \\ & \times \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{Bmatrix} I_1 & I_1 & I'' \\ K & I & I_1 \end{Bmatrix} \begin{Bmatrix} F & I'' & J \\ K & J & I \end{Bmatrix} \end{aligned} \quad (15)$$

and with $i \neq j$

$$\begin{aligned} \langle \Omega v J I'' F | \mathcal{H}^{kk'}(i, j) | \Omega v J I F \rangle = \sum_{\Omega' v'} \frac{\varepsilon(-1)^{\Omega'+K}}{E_{\Omega v J} - E_{\Omega' v' J'}} f_k^*(1, \Omega', \Omega) f_k(1, \Omega', \Omega) \sum_K (2K+1) \times \\ \times \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} (-1)^{F+I''} (2J+1) ((2I''+1)(2I+1))^{1/2} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{Bmatrix} I_1 & I & I_1 \\ k & K & k' \\ I_1 & I'' & I_1 \end{Bmatrix} \begin{Bmatrix} F & I'' & J \\ K & J & I \end{Bmatrix}. \end{aligned} \quad (16)$$

In (16), $\varepsilon = 1$ if the two electronic states $|\Omega\rangle$ and $|\Omega'\rangle$ have the same symmetry u or g and $\varepsilon = -1$ if they have opposite symmetry.

5. Discussion of the results. — We would like to discuss the main contributions which correspond to $k = 1$ or 2 and $k' = 1$ or 2.

As already noted, the terms as $\mathcal{H}_{(i,i)}^{kk'}$ are difficult to distinguish from the first order terms \mathcal{H}^k . Indeed if we compare expressions (3) and (15), the term of rank K in (15) has exactly the same dependence in I, I'', J, F as the first-order term \mathcal{H}^k for $k = K$ in (3). If $K = 0$, the corresponding term is independent of I and F ($I'' = I$) and has no interest, all the hyperfine sublevels being shifted by the same amount.

On the contrary, the cross term $\mathcal{H}_{(i,j)}^{kk'}$ gives tensor components of rank K which can indeed be distinguished from the first order terms of the same rank $k = K$. The $\mathcal{H}_{(i,j)}^{kk'}$ term involves a 9j symbol which is absent in the direct \mathcal{H}^k term. In the present case, the term corresponding to $K = 0$ has a dependence in I .

Table III summarizes all the terms which appear when $k = 1$ and 2 and $k' = 1$ and 2.

It must be noted that some terms involving nucleus 1 and nucleus 2 vanish. Indeed the 9j symbol

$$\begin{Bmatrix} I_1 & I'' & I_1 \\ k & K & k \\ I_1 & I & I_1 \end{Bmatrix},$$

TABLE III

This table gives all the terms appearing in the second order perturbation theory

Origin of the terms	Rank K of the tensor operators $Q_{(I)}^K \cdot Q_{(J)}^K$	I, I'', J, F dependence	Terms non vanishing for $\Omega = 0$ states
$\mathcal{U}\mathcal{H}_{\text{MD}}$	1	the same as \mathcal{H}_{MD}	+
$\mathcal{U}\mathcal{H}_{\text{EQ}}$	2	the same as \mathcal{H}_{EQ}	+
$\mathcal{U}\mathcal{H}_{\text{MD}}$	3	the same as \mathcal{H}_{MO}	+
	0	independent	+
$\mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{MD}}(i)$	1	the same as \mathcal{H}_{MD}	
	2	the same as \mathcal{H}_{EQ}	+
$\mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{EQ}}(i) +$ $+ \mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{MD}}(i)$	1	the same as \mathcal{H}_{MD}	
	2	the same as \mathcal{H}_{EQ}	+
	3	the same as \mathcal{H}_{MD}	
	0	independent	+
$\mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{EQ}}(i)$	1	the same as \mathcal{H}_{MD}	
	2	the same as \mathcal{H}_{EQ}	+
	3	the same as \mathcal{H}_{MD}	
	4	the same as \mathcal{H}_{EH}	+
$i \neq j$	0	proportional to $\mathbf{I}_1 \cdot \mathbf{I}_2$	
$\mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{MD}}(j)$	2	the same as the direct spin-spin $\mathcal{H}_{I_1 I_2}$	
$\mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{EQ}}(j)$	1	different of any first order terms	
$\mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{MD}}(j)$	3	—	
	0	—	+
$\mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{EQ}}(j)$	2	—	+
	4	—	+

is equal to zero if K is odd, I and I'' having the same parity. Similarly, $\begin{Bmatrix} I_1 & I'' & I_1 \\ k & K & k' \\ I_1 & I & I_1 \end{Bmatrix} + \begin{Bmatrix} I_1 & I'' & I_1 \\ k' & K & k \\ I_1 & I & I_1 \end{Bmatrix}$ is equal to zero if $K + k + k'$ is odd. For example if $k = k' = 1$, the non vanishing terms in $\mathcal{H}^{kk'}(i, j)$ correspond to $K = 0, 2$; if $k = 1, k' = 2$ or $k = 2, k' = 1$, they correspond to $K = 1, 3$, etc.

Moreover, since $\begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix}$ is equal to zero if

$\Omega = 0$ and K is odd, the terms corresponding to odd values of K are absent in this case.

In principle, all the terms of different rank K but originating from the same terms of the Hamiltonian are related by simple algebraic relations. This is clear from formula (15) and (16). For example, let us discuss the two terms of rank 0 and 2 arising from $\mathcal{H}_{\text{MD}}(i)$, $\mathcal{H}_{\text{MD}}(j)$ with $i \neq j$ in a state $\Omega = 0$. The corresponding matrix elements can be written following the notation of Bunker [5] :

$$\begin{aligned} \langle \Omega = 0, J, I'', F | \mathcal{H}_{(1,2)}^{11} + \mathcal{H}_{(2,1)}^{11} | \Omega = 0, J, I, F \rangle = \\ = \frac{\delta}{2} \delta_{I''} [I(I+1) - 2I(I_1+1)] + d_E I_1(I_1+1)(2I_1+1)(-1)^{I''+F+1} [30(I+1)(I''+1)]^{1/2} \times \\ \times (2J+1) \begin{pmatrix} J & J & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & I'' & J \\ 2 & J & I \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I'' & 2 \end{Bmatrix} \end{aligned} \quad (17)$$

δ represents the scalar spin-spin interaction ($\delta \mathbf{I}_1 \cdot \mathbf{I}_2$) and d_E the tensorial spin-spin interaction

$$\begin{aligned} (d_E(\mathbf{I}_1 \mathbf{I}_2 - 3(\mathbf{I}_1 \cdot \mathbf{r}_{12})(\mathbf{I}_2 \cdot \mathbf{r}_{12})/r_{12}^2)) \\ \delta = \sum_{\Omega'v'} \frac{\varepsilon |f_1(1, \Omega', 0)|^2}{E_{\Omega v J} - E_{\Omega'v'J'}} \frac{2}{3 I_1(I_1+1)(2I_1+1)} \\ d_E = \sum_{\Omega'v'} \frac{\varepsilon |f_1(1, \Omega', 0)|^2}{E_{\Omega v J} - E_{\Omega'v'J'}} \frac{(3\Omega'^2 - 2)}{3 I_1(I_1+1)(2I_1+1)} \end{aligned}$$

The relationship between δ and d_E depends upon the perturbing states. Table IV gives the results for the different possible cases :

TABLE IV

The studied level is a 0_u^+ level. We assumed

$$E_{\Omega v} - E_{\Omega'v'} < 0. \quad \text{If } E_{\Omega v} - E_{\Omega'v'} > 0,$$

all the signs in columns 2 and 3 are changed.

Perturbing level	Sign of δ	Sign of d_E	Relationship between δ and d
1_u	< 0	< 0	$\delta = 2d$
0_u^-	< 0	> 0	$\delta = -d$
1_g	> 0	> 0	$\delta = 2d$
0_g^-	> 0	< 0	$\delta = -d$

Evidently if several perturbing states interact, the relationship between δ and d_E may be difficult to infer *a priori*. However, from the experimental results, it is in principle possible to know the nature of the perturbing state or states.

Finally a further point must be noted. The method used here for the calculation (the separation between the term $\mathcal{H}_{(1,1)}^{kk'}$ or $\mathcal{H}_{(2,2)}^{kk'}$ and the terms $\mathcal{H}_{(1,2)}^{kk'}$ or $\mathcal{H}_{(2,1)}^{kk'}$) presents an apparent difficulty :

The summation on I' is made through intermediate eigenstates $|\Omega' v' J' I' F\rangle$ which may violate the Pauli principle. It is clear that the total contribution of such states which do not exist must be zero. This is insured by relations (1). However, for $\mathcal{H}_{(1,2)}^{kk'}$ alone this contribution is not zero, neither for $\mathcal{H}_{(1,1)}^{kk'}$ etc... It is zero only for $\mathcal{H}_{(1,1)}^{kk'} + \mathcal{H}_{(2,2)}^{kk'} + \mathcal{H}_{(1,2)}^{kk'} + \mathcal{H}_{(2,1)}^{kk'}$. This method enables the calculation of the effective Hamiltonian to be made without knowing the perturbing states.

6. Effective hyperfine Hamiltonian in the $B^3\Pi_{0+}$ state of molecular iodine. — Some precise results have been recently published [9], [10], [14], [16] concerning the hyperfine structure of some levels of the I_2 B and X states. It seems interesting to apply our formalism to these experimental results. As both of these states verify $\Omega = 0$, the theory is the same for the two states but the second-order terms of the perturbation theory are necessary only for the B state because the perturbing states are very much closer.

6.1 FIRST-ORDER TERMS. — As already noted, when $\Omega = 0$, $\mathcal{H}^k(i)$ is different of zero only if k is even. Therefore :

$$\begin{aligned} \langle {}^3\Pi_{0+}, J, I'' F | \mathcal{H}_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2) | {}^3\Pi_{0+}, J, I, F \rangle = 0 \\ \langle {}^3\Pi_{0+}, J, I'' F | H_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2) | {}^3\Pi_{0+}, J, I, F \rangle = 0. \end{aligned}$$

The nonvanishing first order terms are the electric quadrupole and hexadecapole interactions for

$\mathcal{H}_{\text{hf}}(1) + \mathcal{H}_{\text{hf}}(2)$. Their matrix elements are given in table Va.

The first order terms of $\mathcal{H}_{\text{hf}}(1, 2)$ are nonzero

(even if their order is odd). The magnetic dipolar interactions $\mathcal{H}_{IR}(1, 2)$ and $\mathcal{H}_{I_1 I_2}(1, 2)$ have the following matrix elements

$$\begin{aligned} \langle {}^3\Pi_{0+}, J, I'', F | \mathcal{H}_{IR}(1, 2) | {}^3\Pi_{0+}, J, I, F \rangle &= \delta_{I'', I} \frac{C_D}{2} (F(F+1) - I(I+1) - J(J+1)) \\ \langle {}^3\Pi_{0+}, JI'' F | \mathcal{H}_{I_1 I_2}(1, 2) | {}^3\Pi_{0+}, JIF \rangle &= d_D I_1(I_1+1)(2I_1+1)(-1)^{I''+F+1} (30(2I+1) \\ &\quad \times (2I''+1))^{1/2} (2J+1) \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & J & I \\ 2 & I'' & J \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I'' & 2 \end{Bmatrix}. \end{aligned}$$

The matrix elements of $\mathcal{H}_{\text{EQ}}(1, 2)$ are, inside an electronic state, proportional to those of $\mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2)$. Usually the two terms are not distinguished, the usual eqQ constant including both of them.

We should take into account also the matrix elements of $\mathcal{H}_{O_1 D_2} + \mathcal{H}_{D_1 O_2}$ and $\mathcal{H}_{Q_1 Q_2}$ etc... As shown in table I these terms are negligible.

6.2 SECOND ORDER TERMS. — We are now going to treat the terms resulting from the second-order perturbation theory. The perturbing terms are \mathcal{V} ,

$$\mathcal{H}_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2), \mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2),$$

and

$$\mathcal{H}_{\text{MO}}(1) + \mathcal{H}_{\text{MO}}(2).$$

For the $B^3 \Pi_{0+}$ state, \mathcal{V} is the off-diagonal part of the rotational Hamiltonian :

$$\mathcal{V} = -\frac{\hbar^2}{2\mu r_{12}^2} [J_+(L_- + S_-) + J_-(L_+ + S_+)]$$

\mathcal{V} cannot couple u and g states neither $\Omega = 0$ and $\Omega' = 0$ states. Therefore it can only couple the 0_u^+ state to an 1_u state. The matrix element is :

$$\begin{aligned} \langle 1_u v' JIF | \mathcal{V} | 0_u^+ v JIF \rangle &= \\ &= \sqrt{2J(J+1)} \left\langle 1_u v' \left| \frac{\hbar^2}{2\mu r_{12}^2} T_1^1(\mathbf{L}) + T_1^1(\mathbf{S}) \right| 0_u^+ v \right\rangle \\ &= -\sqrt{2J(J+1)} f_0(1_u, 0_u^+). \end{aligned}$$

The order of magnitude of \mathcal{V} is 1 000 MHz for $J = 1$, and \mathcal{V} is linear in J . $\mathcal{H}_{\text{MD}}(i)$ and $\mathcal{H}_{\text{EQ}}(i)$ are of the order of 1 000 MHz. $\mathcal{H}_{\text{hf}}(1, 2)$ is essentially diagonal with respect to the electronic eigenstates and has no effect in these second order terms. $\mathcal{H}_{\text{MO}}(i)$ and $\mathcal{H}_{\text{EH}}(i)$ are too small to be considered in a second order theory; however, since $\mathcal{H}_{\text{MO}}(i)$ has no first order term, we consider the cross term $\mathcal{V} - \mathcal{H}_{\text{MO}}(i)$ which is the biggest term involving $\mathcal{H}_{\text{MO}}(i)$.

α) *Terms of the form $\mathcal{V} - \mathcal{H}^k(i)$.* — The cross term $\mathcal{V} - (\mathcal{H}_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2))$ gives an effective dipolar magnetic term which can be written $C_E \mathbf{I} \cdot \mathbf{J}$. Its matrix elements are proportional to those of $\mathcal{H}_{IR}(1, 2)$.

The matrix elements of the cross term

$$\mathcal{V} - (\mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2))$$

are proportional to the first order term arising from $\mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2)$. They are included in the same term. As this term is proportional to J , this gives a dependence in J to « eqQ ».

The cross term $\mathcal{V} - (\mathcal{H}_{\text{MO}}(1) + \mathcal{H}_{\text{MO}}(2))$ gives an effective octupole oO whose matrix elements are proportional to those of the first order term $\mathcal{H}_{\text{MO}}(1, 2)$. $oO = (oO)_E + (oO)_D$. In fact $(oO)_D$ is negligible (see table I).

β) *Cross terms $\mathcal{H}^k \mathcal{H}^{k'}$.* — We limit our investigations here to k and $k' \leq 2$. As shown in table III, many terms arise. But as $\Omega = 0$, only the terms with even values of K do not vanish.

The terms $\mathcal{H}_{(i,i)}^{kk'}$, which involve the same nucleus twice, may be included in the electric quadrupole or hexadecapole first order term (depending if $K = 2$, or 4), as their matrix elements have the same I, I', J, F dependence.

We are going therefore to focus our attention on the $\mathcal{H}_{(i,j)}^{kk'}$ which involves both nuclei.

i) $k = k' = 1$. This is the second order magnetic dipole Hamiltonian. Its contribution has been given down in formula (17). The term with the δ constant is alone of its kind but the term with d_E can be grouped with the $\mathcal{H}_{I_1 I_1}(1, 2)$ term which has the same $II'' JF$ dependence.

ii) $k = 1, k' = 2$ or $k = 2, k' = 1$. There is no contribution from these terms when $\Omega = 0$ as is shown in table III.

iii) $k = k' = 2$. This is the second order electric quadrupole Hamiltonian. Three terms arise corresponding to $K = 0, 2, 4$. They are given in tables Va and Vb with the constants e, f, h . The constant h has two origins, that noted here and the direct interaction between the two quadrupoles of the two nuclei $\mathcal{H}_{Q_1 Q_2}$. Therefore $h = h_E + h_D$. In fact h_D is negligible (see table I). The effective hyperfine Hamiltonian resulting from all these effects is given in table Va.

TABLE Va

Effective hyperfine Hamiltonian. We have taken into account the fact that I and I'' have the same parity

Origin of the terms	Rank K	Matrix element $\langle {}^3\Pi_0^+ I'' JF \mathcal{H}_{\text{hf}} \text{ effective} {}^3\Pi_0^+ I JF \rangle$
$\left. \begin{array}{l} \mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2) \\ \mathcal{H}_{\text{EQ}}(1, 2) \\ \mathcal{V}(\mathcal{H}_{\text{EQ}}(1) + \mathcal{H}_{\text{EQ}}(2)) \\ \mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{EQ}}(i) \\ \mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{EQ}}(i) \\ \mathcal{H}_{\text{MD}}(i) \mathcal{H}_{\text{MD}}(i) \\ \mathbf{H}_{\text{IR}}(1, 2) \\ \mathcal{V}(\mathcal{H}_{\text{MD}}(1) + \mathcal{H}_{\text{MD}}(2)) \end{array} \right\}$	$\left. \begin{array}{l} 2 \\ 1 \end{array} \right\}$	$\left\{ \begin{array}{l} \ll eqQ \gg (-1)^{2I_1+F} \left(\frac{(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} \right)^{1/2} ((2I+1)(2I''+1))^{1/2} \times \\ \times (2J+1) \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 2 & I_1 & I_1 \\ I_1 & I'' & I \end{Bmatrix} \begin{Bmatrix} F & J & I \\ 2 & I'' & J \end{Bmatrix} \\ \\ \frac{C}{2} \delta_{I''I} (F(F+1) - I(I+1) - J(J+1)) \end{array} \right.$
$\mathcal{H}_{\text{MD}}(1) \mathcal{H}_{\text{MD}}(2)$	0	$\frac{\delta}{2} \delta_{I''I} (I(I+1) - 2I_1(I_1+1))$
$\left. \begin{array}{l} \mathcal{H}_{I_1 I_2}(1, 2) \\ \mathcal{H}_{\text{MD}}(1) \mathcal{H}_{\text{MD}}(2) \end{array} \right\}$	2	$\left\{ \begin{array}{l} d(-1)^{I''+F+1} (I_1(I_1+1)(2I_1+1)) (30(2I+1)(2I''+1))^{1/2} \times \\ \times (2J+1) \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & J & I \\ 2 & I'' & J \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I'' & 2 \end{Bmatrix} \end{array} \right.$
$\mathcal{H}_{\text{EQ}}(1) \mathcal{H}_{\text{EQ}}(2)$	0	$e\delta_{I''} \frac{(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} (-1)^{I+2I_1} \begin{Bmatrix} I & I_1 & I_1 \\ 2 & I_1 & I_1 \end{Bmatrix}$
$\mathcal{H}_{\text{EQ}}(1) \mathcal{H}_{\text{EQ}}(2)$	2	$\left\{ \begin{array}{l} f \frac{(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} \times (-1)^{I''+F} (2J+1) ((2I+1)(2I''+1))^{1/2} \times \\ \times \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & I'' & J \\ 2 & J & I \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 2 \\ I_1 & I_1 & 2 \\ I & I'' & 2 \end{Bmatrix} \end{array} \right.$
$\left. \begin{array}{l} \mathcal{H}_{\text{EQ}}(1) \mathcal{H}_{\text{EQ}}(2) \\ \mathcal{H}_{Q_1 Q_2} \end{array} \right\}$	4	$\left\{ \begin{array}{l} h \frac{(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} \times (-1)^{I''+F} (2J+1) ((2I+1)(2I''+1))^{1/2} \times \\ \times \begin{pmatrix} J & 4 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & I'' & J \\ 4 & J & I \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 2 \\ I_1 & I_1 & 2 \\ I & I'' & 4 \end{Bmatrix} \end{array} \right.$
$\mathcal{V}(\mathcal{H}_{\text{OM}}(1) + \mathcal{H}_{\text{OM}}(2))$	3	$\left\{ \begin{array}{l} \frac{oO}{\begin{pmatrix} I_1 & I_1 & 3 \\ I_1 & -I_1 & 0 \end{pmatrix}} (-1)^{1+2I_1+F} (2J+1) \sqrt{2J(J+1)} ((2I+1)(2I''+1))^{1/2} \times \\ \times \begin{pmatrix} J & 3 & J \\ -1 & 1 & 0 \end{pmatrix} \begin{Bmatrix} F & I'' & J \\ 3 & J & I \end{Bmatrix} \begin{Bmatrix} 3 & I_1 & I_1 \\ I_1 & I'' & I \end{Bmatrix} \end{array} \right.$
$\left. \begin{array}{l} \mathcal{H}_{\text{EH}}(1) + \mathcal{H}_{\text{EH}}(2) \\ \mathcal{H}_{\text{EQ}}(i) \mathcal{H}_{\text{EQ}}(i) \end{array} \right\}$	4	$\left\{ \begin{array}{l} \frac{hH}{\begin{pmatrix} I_1 & I_1 & 4 \\ I_1 & -I_1 & 0 \end{pmatrix}} (-1)^{2I_1+F} (2J+1) ((2I+1)(2I''+1))^{1/2} \times \\ \times \begin{pmatrix} J & 4 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & I'' & J \\ 4 & J & I \end{Bmatrix} \begin{Bmatrix} 4 & I_1 & I_1 \\ I_1 & I'' & I \end{Bmatrix} \end{array} \right.$

The expression of the various constants which appear is given in table Vb.

6.3 COMMENT AND COMPARISON WITH EXPERIMENTAL RESULTS. — α) The « eqQ » constant. — It appears

clearly that the quadrupole coupling constant « eqQ » is contaminated by various terms.

The observed value of « eqQ » in the $B^3\Pi_{0+}$ state of I_2 is about 500 MHz [10]. The two main contri-

TABLE Vb

Expression of the various constants.

$$\begin{aligned}
\ll eqQ \gg &= eqQ + \sum_{v'1u} \frac{-2(f_0(1_u, 0_u^+) f_2(1, 0_u^+, 1_u) + \text{c.c.})}{E_{0^+vJ} - E_{1uv'J}} \times \frac{\sqrt{J(J+1)} \begin{pmatrix} J & 2 & J \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} I_1 & I_1 & 2 \\ I_1 & -I_1 & 0 \end{pmatrix}}{\begin{pmatrix} J & J & 2 \\ 0 & 0 & 0 \end{pmatrix}} + \\
&+ \sum_{k', k=1,2} \sum_{v'\Omega'} (-1)^{2I_1+\Omega'} \frac{2 f_k(1, \Omega', 0_u^+) f_k^*(1, \Omega', 0_u^+)}{E_{0^+vJ} - E_{1uv'J}} \\
&\times \left\{ \begin{matrix} I_1 & 2 & I_1 \\ k & I_1 & k \end{matrix} \right\} \begin{pmatrix} k & k' & 2 \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} I_1 & I_1 & 2 \\ I_1 & -I_1 & 0 \end{pmatrix} \\
C &= C_D + C_E \\
C_E &= - \sum_{v'1u} \frac{f_0(1_u, 0_u^+) f_1(1, 0_u^+, 1_u) + \text{c.c.}}{(E_{0^+vJ} - E_{1uv'J}) \sqrt{I_1(I_1+1)} (2I_1+2)} \\
\delta &= \sum_{\Omega'v'} \frac{2\varepsilon |f_1(1, \Omega', 0_u^+)|^2}{E_{0^+vJ} - E_{\Omega'v'J}} \frac{1}{3 I_1(I_1+1) (2I_1+1)} \\
d &= d_D + d_E \\
d_E &= \sum_{\Omega'v'} \frac{\varepsilon |f_1(1, \Omega', 0)|^2}{E_{0^+vJ} - E_{\Omega'v'J}} \frac{(3\Omega'^2 - 2)}{3 I_1(I_1+1) (2I_1+2)} \\
e &= \sum_{\Omega'v'} \frac{2\varepsilon |f_2(1, \Omega', 0_u^+)|^2}{E_{0^+vJ} - E_{\Omega'v'J}} \frac{\begin{pmatrix} I_1 & I_1 & 2 \\ I_1 & -I_1 & 0 \end{pmatrix}^2}{5} \\
f &= \sum_{\Omega'v'} \frac{2\varepsilon |f_2(1, \Omega', 0_u^+)|^2}{E_{0^+vJ} - E_{\Omega'v'J}} (-1)^{\Omega'} \begin{pmatrix} 2 & 2 & 2 \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} I_1 & I_1 & 2 \\ I_1 & -I_1 & 0 \end{pmatrix}^2 \\
h &= h_E + h_D \\
h_E &= \sum_{\Omega'v'} \frac{2\varepsilon |f_2(1, \Omega', 0_u^+)|^2}{E_{0^+vJ} - E_{\Omega'v'J}} (-1)^{\Omega'} \begin{pmatrix} 2 & 2 & 4 \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} I_1 & I_1 & 2 \\ I_1 & -I_1 & 0 \end{pmatrix}^2 \\
oO &= oO_E + oO_D \\
oO_E &= - \sum_{\Omega'v'} \frac{2(f_0(1_u, 0_u^+) f_3(1, 0_u^+, 1_u) + \text{c.c.})}{E_{0^+vJ} - E_{1uv'J}} \begin{pmatrix} I_1 & I_1 & 3 \\ I_1 & -I_1 & 0 \end{pmatrix} \\
\ll hH \gg &= h\mathcal{H} + \sum_{\Omega'v'} (-1)^{\Omega'+2I_1} \frac{2 |f_2(1, \Omega', 0_u^+)|^2}{E_{0^+vJ} - E_{1uv'J}} \times \\
&\times \left\{ \begin{matrix} I_1 & 4 & I_1 \\ 2 & I & 2 \end{matrix} \right\} \begin{pmatrix} 2 & 2 & 4 \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} I_1 & I_1 & 4 \\ I_1 & -I_1 & 0 \end{pmatrix}
\end{aligned}$$

butions are $\mathcal{H}_{EQ}(1) + \mathcal{H}_{EQ}(2)$ and $\mathcal{H}_{EQ}(1, 2)$, the latter being evaluated at about 30 MHz (see table I).

The « eqQ » is also contaminated by terms due to several sources. The contamination due to $\mathcal{H}_{MD}(i) - \mathcal{H}_{MD}(i)$ is of the order of d_E (see formulas (15) and (16) and tables V) and $d_E \approx 100$ kHz [5], [10]. The contamination by $\mathcal{H}_{EQ}(i) - \mathcal{H}_{EQ}(i)$ should probably be of the same order of magnitude. The contamination

by $\mathcal{V} - (\mathcal{H}_{EQ}(1) + \mathcal{H}_{EQ}(2))$ depends on J and should have also the same order of magnitude for $J = 1$ (as for $J = 1$, $\mathcal{V} \approx \mathcal{H}_{MO} \approx \mathcal{H}_{EQ}$).

The decontamination of « eqQ » would need a precise study of this quantity as a function of v and J . However the first order term « eqQ » could also present some dependence in v and J , and the contamination will be very difficult to observe.

β) *The $C = C_E + C_D$ constant.* — The C_D constant can be easily evaluated

$$C_D \approx 0.15 \text{ kHz}.$$

This value is very small, and almost negligible.

C has been measured [9] in the B state for about 10 vibrational levels and is of the order of 30 kHz for low v values. It increases drastically with v and reaches 950 kHz for $v = 62$. This is interpreted as a perturbation by a dissociative state having the same dissociation limit as the B state.

A theory of this effect has been published [9] and the observed values of C are rather well represented by the formula

$$C(\text{kHz}) = \frac{1.3 \times 10^5}{E_c - E_v}$$

where E_v (cm^{-1}) is the vibrational energy inside the B state; E_c is an energy very close to the dissociation limit of the B state ($E_c = 4\,400 \text{ cm}^{-1}$).

The perturbing state responsible for C_E is necessarily a 1_u state because \mathcal{U} does not couple $\Omega = 0$ to $\Omega = 0$ states, neither u to g states. It is most probably the $^3\Sigma_{1u}^+$ state of configuration 1 441 or the $^3\Sigma_{1u}^+$ state of configuration 2 332 of reference [15] (see Fig. 1 of this reference). The Landé factors and the chemical shifts g_1 of the levels of the $B^3\Pi_{0u}$ state of I_2 are also interpreted as due to the same perturbing states.

γ) *The $d = d_D + d_E$ constant.* — d_D is also evaluated to have a very low value of :

$$d_D = 0.15 \text{ kHz}.$$

d_E has been measured only for two vibrational levels, $v' = 11$ and $v' = 43$ of the B state. The results are given in table VI. If the perturbing state for d_E is the same as for C_E , the ratio d_E/C_E must be approximately constant. This ratio can be estimated :

$$\frac{d_E}{C_E J} \approx \frac{\mathcal{H}_{DM}}{\mathcal{U}} \approx \frac{1}{J}.$$

At the present level of accuracy, this relation seems to be well verified.

However, this verification is not really conclusive as there are only two experimental results. As \mathcal{H}_{MD} can couple the $^3\Pi_{0u}$ state not only to 1_u states but also to 0_u^- , 0_u^+ and 1_g states, the d_E term may be due to states other than the 1_u responsible for C_E . In this case,

there should not be any relationship between C_E and d_E .

δ) *The δ constant.* — The δ constant has been measured on the same levels as d and the results are given in table VI. We have shown in table IV that the perturbation of a 0_u^+ state by a 1_u state lying above in energy gives the results $\delta < 0$, $d < 0$ and $\delta = 2 d_E$.

The ratios δ/d_E given in table V are very different from 2. If we suppose that the B state is perturbed not only by a 1_u state but also by a 0_g^- state lying above in energy, then δ and d_E are sums of two terms, of opposite sign for δ , of the same sign for d_E . Such an hypothesis, which explains the *anomalous* δ/d_E value could be confirmed with more experimental results.

Finally, all the calculations made have not considered the terms involving the e , f , h constants. This may have changed the δ and d values which were obtained by a least squares fit method.

ε) *The e , f , h constants.* — To our knowledge, they have never been considered until now in the literature although in the case of the B state of I_2 , they must be of the order of magnitude of δ and d . This results from the fact that $\mathcal{H}_{EQ} \approx \mathcal{H}_{DM}$. The calculations made to interpret the hyperfine structure should try to take into account these 3 new terms. The only real limitation to do this lies in the following fact :

The hyperfine structure of the ground and the excited states are extracted from a spectrum consisting of 15 or 21 intense lines at most. With this limited information, it is difficult to fit too high a number of constants.

η) *The magnetic octupole $oO = (oO)_E$.* — This term arises from $\mathcal{U} - (\mathcal{H}_{MO}(1) + \mathcal{H}_{MO}(2))$ perturbation. We can estimate the $(oO)_E$ term by using the values of C_E , as the perturbing state is necessarily the 1_u because \mathcal{U} is involved here :

$$\frac{C_E}{(oO)_E} \approx \frac{\mathcal{H}_{MD}}{\mathcal{H}_{MO}}.$$

We can estimate \mathcal{H}_{MO} and \mathcal{H}_{MD} from the measurements done in the iodine atom ground state $^2P_{3/2}$ [11]

$$\mathcal{H}_{MO} \approx 2 \text{ kHz}$$

$$\mathcal{H}_{MD} \approx 10^3 \text{ MHz}.$$

We deduce : $(oO)_E \approx 2 \times 10^{-6} C_E$.

TABLE VI

C_E , d_E and δ values for the two levels $v = 11$ and $v = 43$. The results are taken from the papers of Landsberg [14].

	C_E (kHz)	d_E (kHz)	δ (kHz)	$\frac{C_E}{d_E}$	$\frac{\delta}{d_E}$
$v = 11$	28.8 ± 1.4	-25.6 ± 2.8	-11.7 ± 1.6	~ 1.2	$\sim +0.5$
$v = 43$	186.9 ± 0.6	-102.5 ± 0.7	-3.36 ± 0.55	~ 1.8	$\sim +0.03$

For instance, in the level $v' = 43$, $J' = 12$, C_E has been measured [10], [14], $C_E = 180$ kHz. Therefore the order of magnitude of $(oO)_E$ is 0.5 Hz.

Ezekiel *et al.* [10], [16] have published a measurement of oO in this level (let us note that their Hamiltonian was not quite correct). Their result is 1 or 2 kHz depending on the publication [10], [16]. Our estimate is rough, but the result of Ezekiel *et al.* seems unrealistic.

ξ) *The $h\mathcal{H}$ term.* — This term contains two contributions : the first order term of the hexadecapole interaction, and the second order quadrupole interaction. From tables III and V and formulas (15) and (16), it is evident that this last term is of the order of magnitude of the e, f, h constants. The direct hexadecapole term is difficult to estimate as it cannot be measured in the $^2P_{3/2}$ state of the ^{127}I atom ($J = 3/2$). As it results from the evaluation carried in table I, the order of magnitude of the direct hexadecapole interaction could be 1 kHz.

7. Conclusion. — We have derived the effective hyperfine Hamiltonian for a homonuclear diatomic molecule in a Hund's case a representation. The results are summarized in formulae (15) and (16) and in table III. All the terms originating from the same terms of the Hamiltonian are related. The relation between them depends on the nature of the perturbing

states : if the perturbing states are known, this relation is easily calculable (see formulae (15) and (16)). If they are unknown, the experimental values of the various term give precise information concerning the possible nature of the perturbing states as is illustrated in the case of the ratio δ/d .

Finally, all these theoretical results are applied to the $B^3\Pi_{0+}$ state of I_2 . From the experimental values of the related δ and d constants, hypotheses are formulated about the perturbing states. The terms arising from the second order quadrupole Hamiltonian are introduced (constants e, f and h). Up to now these constants e, f and h have never been considered but they can be of the same order of magnitude as δ and d . In contradiction with recent papers [10], [16], we conclude that with the present precision of the experimental results, it is impossible to observe a magnetic octupole interaction in the B state of I_2 . On the contrary, it could be possible to observe e, f, h and even $h\mathcal{H}$ the hexadecapole term. It is not clear *a priori* that e, f and h are negligible compared to d and δ . If they are, it could probably be proved by a computer fit. However the presently available experimental results are insufficient since only two levels have been studied with high accuracy. A systematic study of the hyperfine structure in the B state as a function of v and J would be necessary to clarify definitively this problem.

Appendix I. — EXACT CALCULATION OF FORMULAE (15) AND (16). — In order to perform this calculation, we define two irreducible tensor operator basis sets $\frac{J'J}{J}T_q^k$ and ${}_{II}T_q^k$ where the first operate on the orbital coordinates of the electrons and of the nuclei and the second on nuclear spin coordinates.

$\frac{J'J}{J}T_q^k$ has non vanishing matrix element only between states $\langle \Omega' J' |$ and $| \Omega J \rangle$, and ${}_{II}T_q^k$ only between states $\langle (I_1 I_2) I' |$ and $| (I_1 I_2) I \rangle$.

They are orthonormalized as follows :

$$T \frac{J'J}{J}T_q^k(\frac{J'J}{J}T_q^k)^+ = \delta_{\Omega\Omega'} \delta_{\Omega_1\Omega_1'} \delta_{JJ_1} \delta_{J'J_1'} \delta_{kk_1} \delta_{qq_1}$$

and

$$T {}_{II}T_q^k({}_{II}T_q^k)^+ = \delta_{I_1I_1'} \delta_{I_2I_2'} \delta_{kk_1} \delta_{qq_1}. \quad (\text{A.1})$$

The matrix elements of the scalar product $\sum_q (-1)^q \frac{J'J}{J}T_q^k {}_{II}T_{-q}^k$ are obtained by formula 7.1.6 of Edmonds [6] :

$$\left\langle \Omega' J' I' F \left| \sum_q (-1)^q \frac{J'J}{J}T_q^k {}_{II}T_{-q}^k \right| \Omega J I F \right\rangle = (-1)^{J+I'+F} \begin{Bmatrix} F & I' & J' \\ k & J & I \end{Bmatrix} \times \\ \times \langle \Omega' J' | \frac{J'J}{J}T^k | \Omega J \rangle \langle I' | {}_{II}T^k | I \rangle.$$

From the normalization condition it may be shown that :

$$\langle \Omega' J' | \frac{J'J}{J}T^k | \Omega J \rangle = \sqrt{2k+1} \quad \text{and} \quad \langle I' | {}_{II}T^k | I \rangle = \sqrt{2k+1}.$$

If $P_{\Omega v J I}$ is the projector on the subspace $| \Omega v J I \rangle$, $\mathcal{H}^k(i)$, the multipole interaction of rank k for nucleus i can be replaced by :

$$P_{\Omega' v' J' I'} \mathcal{H}^k(i) P_{\Omega v J I} = w_k(i, \Omega', \Omega, J', J, I', I) \sum_q (-1)^q \frac{J'J}{J}T_q^k {}_{II}T_{-q}^k$$

$$w_k(i, \Omega', \Omega, J', J, I', I) = \frac{(-1)^{k+I_1+I_2+I+J}}{(2k+1)} f_k(i, \Omega', \Omega) ((2I+1)(2I'+1)(2J+1)(2J'+1))^{1/2} \times \\ \times \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{Bmatrix} k & I_1 & I_1 \\ I_2 & I' & I \end{Bmatrix}. \quad (\text{A.2})$$

The consequences of relations (1) are :

$$w_k(1, \Omega'_u, \Omega_u, J', J, I', I) = (-1)^{I+I'} w_k(2, \Omega'_u, \Omega_u, J', J, I', I)$$

and

$$w_k(1, \Omega'_g, \Omega_g, J', J, I', I) = (-1)^{I+I'+1} w_k(2, \Omega'_g, \Omega_g, J', J, I', I).$$

We must calculate second-order terms of the type :

$$\langle \Omega v J I'' F | \mathcal{H}^{kk'}(i, j) | \Omega v J I F \rangle = \left\langle \Omega v J I'' F \left| \mathcal{H}^k(i) \right| \sum_{\Omega' v' J' I'} \frac{P_{\Omega' v' J' I'}}{E_{\Omega v J} - E_{\Omega' v' J'}} \left| \mathcal{H}^{k'}(j) \right| \Omega v J I F \right\rangle$$

where i and j represent nucleus 1 or nucleus 2

$$P_{\Omega v J I''} \mathcal{H}^{kk'}(i, j) P_{\Omega v J I} = \sum_{\Omega' v' J' I'} w_k(i, \Omega, \Omega', J, J', I'', I') \\ \frac{w_k(j, \Omega', \Omega, J', J, I', I) \sum_{q q'} (-1)^{q+q'} \frac{\Omega \Omega'}{J J'} T_q^k \frac{\Omega' \Omega}{J' J'} T_{q'}^{k'} I'' I' T_{-q}^k I' I T_{-q'}^{k'}}{E_{\Omega v J} - E_{\Omega' v' J'}}.$$

The product $\frac{\Omega \Omega'}{J J'} T_q^k \frac{\Omega' \Omega}{J' J'} T_{q'}^{k'}$ may be developed on the irreducible tensor operator basis set $\frac{\Omega \Omega}{J J} T_Q^K$.

$$\frac{\Omega \Omega'}{J J'} T_q^k \frac{\Omega' \Omega}{J' J'} T_{q'}^{k'} = \sum_{K Q} T_1(\frac{\Omega \Omega'}{J J'} T_q^k \frac{\Omega' \Omega}{J' J'} T_{q'}^{k'} (\frac{\Omega \Omega}{J J} T_Q^K)^+) \frac{\Omega \Omega}{J J} T_Q^K = \\ = \sum_{K Q} (-1)^{2J'+Q} ((2k+1)(2k'+1)(2K+1))^{1/2} \begin{pmatrix} k' & k & K \\ q' & q & -Q \end{pmatrix} \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} \frac{\Omega \Omega}{J J} T_Q^K.$$

This result is a straightforward application of formula 6.2.8 of Edmonds [6] :

$$I'' I' T_{-q}^k I' I T_{-q'}^{k'} = \sum_{K Q} (-1)^{2I'-Q} ((2k+1)(2k'+1)(2K+1))^{1/2} \times \\ \times \begin{pmatrix} k' & k & K \\ -q' & -q & +Q \end{pmatrix} \begin{Bmatrix} k & k' & K \\ I & I'' & I' \end{Bmatrix} I'' I T_{-Q}^K.$$

Finally after the summation on q and q' , one obtains :

$$P_{\Omega v J I''} \mathcal{H}^{kk'}(i, j) P_{\Omega v J I} = \sum_{\Omega' v' J' I' K} \frac{(-1)^{k+k'+K}}{E_{\Omega v J} - E_{\Omega' v' J'}} (2k+1)(2k'+1) w_k(i, \Omega, \Omega', J, J', I'', I') \times \\ \times w_{k'}(j, \Omega', \Omega, J', J, I', I) \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} \begin{Bmatrix} k & k' & K \\ I & I'' & I' \end{Bmatrix} \sum_Q (-1)^Q \frac{\Omega \Omega}{J J} T_Q^K I'' I T_{-Q}^K. \quad (\text{A.3})$$

1. Summation on I' . — To go further into the calculations, we must differentiate between two types of terms : the terms involving the same nucleus $\mathcal{H}^{kk'}(1, 1)$ or $\mathcal{H}^{kk'}(2, 2)$ and the cross terms $\mathcal{H}^{kk'}(1, 2)$ or $\mathcal{H}^{kk'}(2, 1)$.

1.1 TERMS INVOLVING THE SAME NUCLEUS $\mathcal{H}^{kk'}(i, i)$.

$$P_{\Omega v J I''} \mathcal{H}^{kk'}_{(i'i)} P_{\Omega v J I} = \sum_{\Omega' v' J' I' K} \frac{(-1)^{I+I'+J+J'+K}}{E_{\Omega v J} - E_{\Omega' v' J'}} f_k^*(i, \Omega', \Omega) f_k(i, \Omega', \Omega) (2J+1)(2J'+1) \times \\ \times (2I'+1) \sqrt{(2I+1)(2I''+1)} \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} J' & k' & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{Bmatrix} k & I_1 & I_1 \\ I_2 & I' & I'' \end{Bmatrix} \\ \times \begin{Bmatrix} k' & I_1 & I_1 \\ I_2 & I' & I \end{Bmatrix} \begin{Bmatrix} K & k' & k \\ I' & I'' & I \end{Bmatrix} \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} \sum_Q (-1)^Q \frac{\Omega \Omega}{J J} T_Q^K I'' I T_{-Q}^K. \quad (\text{A.4})$$

(We have used formula (A.2)).

With formula 6.2.12 of Edmonds [6], we may write : ($I_1 = I_2$)

$$\begin{aligned} \sum_{I'} (2I' + 1) (-1)^{I'} \begin{Bmatrix} k & I_1 & I_1 \\ I_1 & I' & I'' \end{Bmatrix} \begin{Bmatrix} k' & I_1 & I_1 \\ I_1 & I' & I \end{Bmatrix} \begin{Bmatrix} k & k' & K \\ I & I'' & I' \end{Bmatrix} = \\ = (-1)^{K+k'+k+I+I''} \begin{Bmatrix} K & I & I'' \\ I_1 & I_1 & I_1 \end{Bmatrix} \begin{Bmatrix} I_1 & K & I_1 \\ k' & I' & k \end{Bmatrix} \\ P_{\Omega v J I''} \mathcal{H}_{(i,i)}^{kk'} P_{\Omega v J I} = \sum_{\Omega' v' J' K} \frac{(-1)^{k+k'+I''+J+J'}}{E_{\Omega v J} - E_{\Omega' v' J'}} f_k^*(1, \Omega', \Omega) f_k(1, \Omega', \Omega) (2J + 1) (2J' + 1) \times \\ \times \sqrt{(2I + 1) (2I'' + 1)} \begin{Bmatrix} K & I & I'' \\ I_1 & I_1 & I_1 \end{Bmatrix} \begin{Bmatrix} I_1 & K & I_1 \\ k' & I_1 & k \end{Bmatrix} \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \\ \times \begin{pmatrix} J' & k' & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} \times \sum_Q (-1)^Q \frac{\Omega\Omega'}{JJ} T_{-Q}^K T_{I'I}^K. \quad (\text{A.5}) \end{aligned}$$

1.2 TERMS INVOLVING THE NUCLEUS 1 AND THE NUCLEUS 2. — For $\mathcal{H}_{(1,2)}^{kk'}$ or $\mathcal{H}_{(2,1)}^{kk'}$ the result is that of expression (A.4) multiplied by $(-1)^{I+I'} \varepsilon$ where $\varepsilon = 1$ if the two electronic states Ω and Ω' have the same symmetry (u or g) and $\varepsilon = -1$ if they have opposite symmetry (Ω'_u and Ω_g or Ω'_g and Ω_u).

Now we use the formula :

$$\begin{aligned} \sum_{I'} (2I' + 1) (-1)^{2I'} \begin{Bmatrix} k & I_1 & I_1 \\ I_1 & I' & I'' \end{Bmatrix} \begin{Bmatrix} k' & I_1 & I_1 \\ I_1 & I' & I \end{Bmatrix} \begin{Bmatrix} k & k' & K \\ I & I'' & I' \end{Bmatrix} = \begin{Bmatrix} I_1 & I & I_1 \\ k & K & k' \\ I_1 & I'' & I_1 \end{Bmatrix} \\ P_{\Omega v J I''} \mathcal{H}_{(i,j)}^{kk'} P_{\Omega v J I} = \sum_{\Omega' v' J' K} \frac{(-1)^{K+J+J'} \varepsilon f_k(1, \Omega', \Omega) f_{k'}(1, \Omega', \Omega)}{E_{\Omega v J} - E_{\Omega' v' J'}} (2J + 1) (2J' + 1) \times \\ \times \sqrt{(2I + 1) (2I'' + 1)} \begin{Bmatrix} I_1 & I'' & I_1 \\ k & K & k' \\ I_1 & I & I_1 \end{Bmatrix} \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} J' & k' & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \\ \times \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} \times \sum_Q (-1)^Q \frac{\Omega\Omega'}{JJ} T_{-Q}^K T_{I'I}^K. \quad (\text{A.6}) \end{aligned}$$

2. **Summation on J' .** — Here we must again differentiate between two situations.

2.1 THE PERTURBING STATES ARE THE NEIGHBOURING ROTATIONAL LEVELS OF THE SAME ELECTRONIC STATE. — $\Omega = \Omega'$ and $v = v'$.

The energy denominator is small and depends drastically upon J' , its sign changes with J' . No simple summation on J' is possible in this case. All the tensorial orders K consistent with $|k - k'| \leq K \leq k + k'$ arise. In fact, our decomposition in irreducible tensor operators has no clear advantage in this case : the electronic reduced matrix elements contained in f_k or $f_{k'}$ are the same arising in the diagonal term of \mathcal{H}^k and $\mathcal{H}^{k'}$. The energy of the perturbing levels are well known. And the exact calculation of the hyperfine splitting is possible without introducing new parameters.

If the perturbing levels are the neighbouring vibrational levels of the same electronic state, the contribution of these levels is very small because $\langle \Omega v' | \Omega v \rangle = 0$ and because the electronic reduced matrix elements of \mathcal{H}_k generally have only a small dependence on r_{12} , the distance of the two nuclei. Depending of the different cases the contribution of these terms may be either neglected or included in the terms of paragraph 2.2.

2.2 THE PERTURBING STATES BELONG TO OTHER ELECTRONIC STATES. — In this case, the energy of the denominator is generally of the order of thousands of cm^{-1} . The summation is performed over the different rotational levels of a given electronic state Ω' . The selection rule is $J - k \leq J' \leq J + k$ if $k \leq k'$ and $J - k' \leq J' \leq J + k'$ if $k' \leq k$ and we will apply our theory to small values of k (1 or 2). Therefore, it seems

reasonable to assume that $E_{\Omega'v'J\pm k} \simeq E_{\Omega'v'J}$. In expression (A.5) or (A.6) $\frac{1}{E_{\Omega vJ} - E_{\Omega'v'J}}$ can be taken out of the summation.

Let us use the formula 2.19 of Rotenberg's book [7] :

$$\begin{aligned} \sum_{J'} (2J' + 1) (-1)^{J'} \begin{pmatrix} J' & k' & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{Bmatrix} k & k' & K \\ J & J & J' \end{Bmatrix} = \\ = (-1)^{\Omega'} \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \quad (J, \Omega, \Omega' \text{ are integers}). \end{aligned}$$

The final results are :

$$\begin{aligned} P_{\Omega vJI''} \mathcal{H}_{(i,i)}^{kk'} P_{\Omega vJI} = \sum_{\Omega'v'} \frac{(-1)^{\Omega'+k+k'+J+I''}}{E_{\Omega vJ} - E_{\Omega'v'J}} f_k^*(1, \Omega', \Omega) f_k(1, \Omega', \Omega) (2J+1) \sqrt{(2I+1)(2I''+1)} \times \\ \times \sum_K \begin{Bmatrix} I_1 & K & I_1 \\ k' & I_1 & k \end{Bmatrix} \begin{Bmatrix} K & I & I'' \\ I_1 & I_1 & I_1 \end{Bmatrix} \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \\ \times \sum_Q (-1)^Q \mathcal{T}_{JJ}^{\Omega\Omega} T_Q^K I'' I T_{-Q}^K \quad (\text{A.7}) \end{aligned}$$

and with $i \neq j$

$$\begin{aligned} P_{\Omega vJI''} \mathcal{H}_{(i,j)}^{kk'} P_{\Omega vJI} = \sum_{\Omega'v'} \frac{(-1)^{\Omega'+k+k'+J(i)}}{E_{\Omega vJ} E_{\Omega'v'J}} f_k^*(1, \Omega', \Omega) f_k(1, \Omega', \Omega) (2J+1) \sqrt{(2I+1)(2I''+1)} \times \\ \times \sum_K \begin{Bmatrix} I_1 & I'' & I_1 \\ k & K & k' \end{Bmatrix} \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \sum_Q (-1)^Q \mathcal{T}_{JJ}^{\Omega\Omega} T_Q^K I'' I T_{-Q}^K. \quad (\text{A.8}) \end{aligned}$$

We recall that :

$$\left\langle \Omega J I'' F \left| \sum_Q (-1)^Q \mathcal{T}_{JJ}^{\Omega\Omega} T_Q^K I'' I T_{-Q}^K \right| \Omega J I F \right\rangle = (-1)^{J+I''+F} (2K+1) \begin{Bmatrix} F & I'' & J \\ K & J & I \end{Bmatrix}.$$

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