

## GENERAL FORM OF THE CENTRIFUGAL TERM IN THE ROTATIONAL SPECTRA\*

By

I. KOVÁCS

DEPARTMENT OF ATOMIC PHYSICS, POLYTECHNICAL UNIVERSITY, BUDAPEST

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The explicit form of the centrifugal term is known so far only for the Hund's limiting cases. The present paper presents its explicit form in the intermediate case between Hund's case a) and b) for terms of any kind.

At the theoretical examination of the structure of the rotational spectra of diatomic molecules several interactions must be taken into consideration simultaneously by means of the perturbation calculation. These are the terms omitted at the separation of the wave equation, the terms of the spin-orbit, spin-spin and rotation-spin interactions, as well as the non-diagonal terms of the centrifugal term. The simultaneous taking into consideration of all these terms would make the final form of the multiplet formulae very complicated. Since the perturbation between the multiplet components and the spin-orbit interaction is commonly larger than the others, it seems suitable to consider first these interactions by means of the perturbation calculation (these give the well-known multiplet formulae) and then the remainder by a method of approach which gives the terms derived from the last interactions in additive form to the multiplet formulae already established. Such a consideration of the spin-spin interaction, as well as the interaction between the rotation and spin is already well known [1],[2]. In the case of the spin-spin interaction a number of the experimental examples showed a good agreement with the theoretical results. In the present paper the same procedure is applied for the case of the centrifugal term. By establishing the form of the centrifugal term for the Hund's case a) and b), as well as the non-diagonal perturbation matrix elements, the form of the centrifugal term may be given in this way in the intermediate cases between Hund's case a) and b), for terms of any kind and multiplicity.

Let  $H_0$  denote the energy operator of the separable wave equation and  $H^p$ , on the one hand, the perturbation operator of the terms of higher order of magnitude neglected at the separation, which describes the perturbation

\* This paper is dedicated to my friend, Academician PÁL GOMBÁS, on the occasion of his sixtieth birthday, as a mark of my high esteem and heartfelt feelings. I wish him all further success in his activities and a long life.

between the components of the same multiplet term, and on the other hand, the perturbation operator of a higher order of magnitude of the spin-orbit interaction.  $\bar{H}^p$  should denote the perturbation operator of the smaller interactions (e.g. centrifugal term, spin-spin or rotation-spin interaction) to be taken into account later.

$$(H' + \bar{H}^p - W_i'') \psi_i'' = 0, \quad (1)$$

where  $H' = H_0 + H^p$  and  $W_i'' = W_i' + \Delta W_i'$ . Here  $\psi_i''$  is the new perturbed wavefunction, and  $W_i'$  the eigenvalue of the operator  $H'$ , and this represents the well-known multiplet formulae. If  $\bar{H}^p$  is small (as according to the experiments the value of the centrifugal term, the spin-spin interaction and interaction between the rotation and spin is small compared with, for instance, the spin-orbit interaction which gives the greatest part of the multiplet splitting) then  $\Delta W_i'$  is also small and no great error is committed if  $\psi_i''$  is replaced by  $\psi_i'$ , the already once perturbed wave function of the operator  $H'$ . Thus, let  $\psi_i'' \approx \psi_i'$ . Then, since

$$(H' - W_i') \psi_i' = 0 \quad (2)$$

with a good approximation it can often be written (1) and (2) that

$$(\bar{H}^p - \Delta W_i') \psi_i' = 0 \quad (3)$$

and

$$\Delta W_i' = \int \psi_i'^* \bar{H}^p \psi_i' d\tau, \quad (4)$$

respectively.

It is known, however, that  $\psi_i' = \sum S_{ik} \psi_k$ , where  $\psi_k$  is the unperturbed wavefunction of the operator  $H_0$  and  $S_{ik}$  the elements of the transformation matrix, arising from taking into account the operator  $H^p$ . The latter are known explicitly for the doublet, triplet, and quartet terms as functions of the rotation quantum number for all kinds of terms. By the use of this (4) can be written

$$\Delta W_i' = \sum_k S_{ik}^* \sum_l S_{lk} \bar{H}_{kl}^p \quad (5)$$

and

$$\bar{H}_{kl}^p = \int \psi_k^* \bar{H}^p \psi_l d\tau. \quad (6)$$

Applied to the spin-spin interaction this formula could, in many cases, excellently interpret the deviations from the usual multiplet formulae even if the terms mentioned belong not to Hund's limiting cases, but to the intermediate case. This can be seen in the cases of the  ${}^3\Pi$  terms of the NH, PH, PF and TiO molecules, respectively, of one  ${}^3\Delta$  term of the CO molecule and of one  ${}^4\Pi$  term of the  $O_2^+$  molecule [3].

As is known, with the increase of the rotation of the molecule the equilibrium nuclear distance becomes greater which is manifested in the apparent decrease of the rotational constant, or an additional term is attached to the energy expression, the form of which in Hund's case b) is as follows:

$$H_b^c(A, N; A, N) = -D\vec{R}^4 = -D[\vec{N}^2 - A^2]^2 = -D[N(N+1) - A^2]^2, \quad (7)$$

where  $N$  is the rotational quantum number in case b),  $A$  is the projection along the molecular axis of the resulting orbital angular momentum, and  $D$  the constant of the centrifugal term. However, (7) is exact only when the electron spin is coupled to the vector  $\vec{N}$ . If we want to follow the process of the suc-

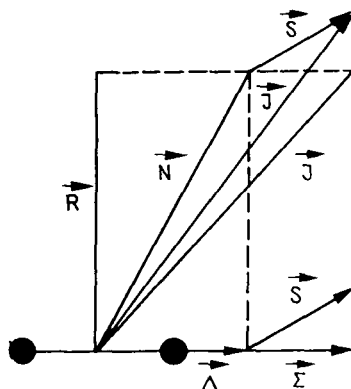


Fig. 1

cessive decoupling from the molecular axis and the coupling to vector  $\vec{N}$ , the perturbation calculation of quantum mechanics has to be employed. This, however, requires a knowledge of the perturbation matrix element. For its calculation let us start from (7) by expressing the vector  $\vec{N}$  by vectors  $\vec{J}$  and  $\vec{S}$ . On the basis of the Figure it can be seen that

$$\begin{aligned} H^c &= -D[\vec{N}^2 - A^2]^2 = -D[(\vec{J} + \vec{S})^2 - A^2]^2 = -D[\vec{J}^2 + \vec{S}^2 - A^2 - 2(\vec{J}\vec{S})]^2 = \\ &= -D[\vec{J}^2 + \vec{S}^2 - A^2 - 2J_z S_z - 2(J_\xi S_\xi + J_\eta S_\eta)]^2 = \\ &= -D\{[\vec{J}^2 + \vec{S}^2 - A^2 - 2J_z S_z]^2 + \\ &\quad + 4(J_\xi S_\xi + J_\eta S_\eta)^2 - 4(\vec{J}^2 + \vec{S}^2 - A^2)(J_\xi S_\xi + J_\eta S_\eta) + \\ &\quad + 4J_z S_z(J_\xi S_\xi + J_\eta S_\eta) + 4(J_\xi S_\xi + J_\eta S_\eta)J_z S_z\}. \end{aligned} \quad (8)$$

In the course of the detailed calculation, by making use of a few of the well-known relationships pertaining to the characteristics of quantum vectors,

the following matrix elements are given which hold good for a term of any multiplicity and type:

$$\begin{aligned} H_a^c(\Omega, \Sigma; \Omega\Sigma) &= -D\{[f(J) + f(S)]^2 + 2f(J)f(S) + 2\Omega\Sigma\}, \\ H_a^c(\Omega, \Sigma; \Omega \pm 1, \Sigma \pm 1) &= -2D\{f(J, \Omega) + f(S, \Sigma) - 1\}\{f(J, \Omega)f(S, \Sigma)\}^{1/2}, \quad (9) \\ H_a^c(\Omega, \Sigma; \Omega \pm 2, \Sigma \pm 2) &= -D\{f(J, \Omega)f(J, \Omega \pm 1)f(S, \Sigma)f(S, \Sigma \pm 1)\}^{1/2}, \end{aligned}$$

where

$$\begin{aligned} f(x) &= x(x+1) - \bar{x}^2, \\ f(x, \bar{x}) &= x(x+1) - \bar{x}(\bar{x} \pm 1), \\ f(x, \bar{x} \pm 1) &= x(x+1) - (\bar{x} \pm 1)(\bar{x} \pm 2), \end{aligned} \quad (9a)$$

and  $\bar{x}$  is the component of  $x$  along the molecular axis. It can be seen that taking into account the decoupling of the spin also modifies the diagonal term corresponding to case a) which has been expressed so far in the form

$$-D[J(J+1) - \Omega^2]^2. \quad (10)$$

Taking into account (9) on the basis of (5) for doublet term leads to the following expression for the centrifugal term in the intermediate case between Hund's cases a) and b)

$$\begin{aligned} H_N^c(J) &= -D\{J_A^2(J_A^2 + 1) + A^2 + \\ &+ 2AJ_A^2(S_{A-1/2, N}^2 - S_{A+1/2, N}^2) - 4S_{A+1/2, N}S_{A-1/2, N}J_A^3\}, \end{aligned} \quad (11)$$

where  $N = J - 1/2$  and  $J + 1/2$ , respectively, the forms of  $S$  are known [4] and

$$J_A^2 = (J + 1/2)^2 - A^2. \quad (11a)$$

(11) is simply to be added to the well-known HILL and VAN VLECK doublet formula. ALMY and HORSFALL [5] have produced (9) for a special case, namely, that of  ${}^2\Pi$  terms, but did not give a solution on the basis of (5), but solved the secular equation supplemented by them (i.e. (9)) directly which broke up the structure of the original HILL and VAN VLECK formula and resulted in a complicated expression difficult to handle. This is further complicated in the case of higher multiplets, and, in addition, if further corrections are taken into account (e.g. spin—spin interaction, rotation—spin interaction), the whole process has to be started again and it is rather difficult to see the actual effects of the respective corrections. These hindrances can be avoided by the application of (5), since the corrections thus calculated are given in an additive way to the well-known multiplet formulae and their respective effects can be studied separately (cf. the result shown at the spin—spin interaction). That these state-

ments are valid can be seen from the fact that with the procedure mentioned for doublet terms GILBERT [6] was not able to supply explicit formulae for the case of  ${}^3\Pi$  terms for centrifugal corrections, only a procedure for determining the multiplet splitting constant  $A$ .

By the use of (5) and (9) the intermediate form of the centrifugal correction valid for all triplet terms can easily be given. This will be

$$H_N^c(J) = S_{A+1,N}^2 H_{A+1,A+1}^c + S_{A,N}^2 H_{A,A}^c + S_{A-1,N}^2 H_{A-1,A-1}^c + \quad (12)$$

$$+ 2 S_{A+1,N} S_{A,1} H_{A+1,A}^c + 2 S_{A,N} S_{A-1,N} H_{A,A-1}^c + 2 S_{A-1,N} S_{A-1,N} H_{A+1,A-1}^c,$$

where  $N = J-1, J, J+1$ , and the elements of  $H^c$  are to be taken from (9), and the explicit forms of  $S$  are already known [7]. (12) is simply to be added to the BUDÓ triplet formula. Substituting  $Y = 0$  into (12) it is transformed into (7), whereas for  $Y \rightarrow \infty$  it supplies the diagonal elements of (9).

The calculation may be carried out in a similar way for a quartet case. Then we obtain:

$$H_N^c(J) = S_{A+3/2,N}^2 H_{A+3/2,A+3/2}^c + S_{A+1/2,N}^2 H_{A+1/2,A+1/2}^c + S_{A-1/2,N}^2 H_{A-1/2,A-1/2}^c + \quad (13)$$

$$+ S_{A-3/2,N}^2 H_{A-3/2,A-3/2}^c + 2 S_{A+3/2,N} S_{A+1/2,N} H_{A+3/2,A+1/2}^c +$$

$$+ 2 S_{A+1/2,N} S_{A-1/2,N} H_{A+1/2,A-1/2}^c + 2 S_{A-1/2,N} S_{A-3/2,N} H_{A-1/2,A-3/2}^c +$$

$$+ 2 S_{A+3/2,N} S_{A-1/2,N} H_{A+3/2,A-1/2}^c + 2 S_{A+1/2,N} S_{A-3/2,N} H_{A+1/2,A-3/2}^c,$$

where  $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$ , and the elements of  $H^c$  are to be taken from (9), while the forms of the  $S$  transformation matrix elements for  ${}^4\Pi$  term are already known [8].

By taking all these into account the complete multiplet formulae can be written as follows:

$$F_N(J) = T_N(J) + H_N^c(J) + H_N^{SS}(J) + H_N^{SR}(J), \quad (14)$$

where  $T_N(J)$  denotes the usual multiplet formula (for doublet term the known HILL and van VLECK, for triplet term the BUDÓ and for quartet term the BRANDT formulae),  $H_N^c(J)$  is the centrifugal correction of a general form given just above,  $H_N^{SS}(J)$  is the general form of the spin - spin interaction and lastly  $H_N^{SR}(J)$  that of the interaction between rotation and spin. All the four terms refer to the intermediate case between Hund's cases a) and b).

Adopting the procedure written here the calculation for the centrifugal term of the intermediate case between Hund's cases b) and d) may also be carried out. From these the forms calculated for the  $p$ - and  $d$ -terms-complexes can be found in the author's book [9].

## REFERENCES

1. I. KOVÁCS, *Acta Phys. Hung.*, **17**, 67, 1964, *Rev. Roum. de Chim.*, **10**, 1173, 1965.
2. I. KOVÁCS, *Opt.-i Spektr. USSR*, **12**, 17, 1962.
3. I. KOVÁCS, *Acta Phys. Hung.*, **12**, 67, 1960 (NH); **13**, 303, 1961 (PH); **18**, 107, 1965 (CO); *Can. J. Phys.*, **42**, 2180, 1964 (PF); *J. Mol. Spectr.*, **18**, 229, 1965 (TiO); Á. BUDÓ and I. KOVÁCS, *Acta Phys. Hung.*, **4**, 273, 1954; I. KOVÁCS and S. WENIGER, *Journ. de Phys.*, **23**, 377, 1962 ( $O_2^+$ ).
4. E. L. HILL and J. H. VAN VLECK, *Phys. Rev.* **32**, 250, 1928.
5. G. ALMY and R. B. HORSFALL, *Phys. Rev.*, **51**, 491, 1937.
6. C. GILBERT, *Phys. Rev.*, **49**, 619, 1936.
7. Á. BUDÓ, *Zs. f. Phys.* **105**, 579, 1937; I. KOVÁCS, *Can. J. Phys.*, **38**, 955, 1960.
8. Á. BUDÓ and I. KOVÁCS, *Phys. Z.*, **65**, 122, 1944.
9. I. KOVÁCS, *Rotational Structure in the Spectra of Diatomic Molecules*. a. p. Akadémiai Kiadó Budapest, and Adam Hilger Ltd., London 1969.

## ОБЩАЯ ФОРМА ЦЕНТРОБЕЖНОГО ЧЛЕНА В РОТАЦИОННОМ СПЕКТРЕ

И. КОВАЧ

## Резюме

Явная форма центробежного члена известна до сих пор только в предельных случаях Гунда. В данной работе дается его явная форма в промежуточном случае между случаем Гунда *a*) и *b*) членов любого вида.