The Rotational Zeeman Effect of Molecules with Low Barrier Internal Rotation.
II. Derivation of the Effective Rotorsional Hamiltonian

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Theoretical expressions for the molecular parameters in the effective rotorsional Hamiltonian in a strong magnetic field are derived from a second order perturbation treatment within the electronic states which was adapted to the presence of a large amplitude internal motion. The technique developed may be of use also in other applications where it should be necessary to go beyond the Born-Oppenheimer approximation. By use of the theoretical expressions it is now possible to use experimentally determined Zeeman data to derive "experimental values" for the molecular electric quadrupole moments, the paramagnetic susceptibilities, the second moments of the electron charge distribution, and the sign of the molecular electric dipole moment also for low barrier molecules.

Introduction

Study of the rotational Zeeman effect of diamagnetic molecules has led to valuable information on electronic ground state properties such as the molecular electric quadrupole moments and the direction of the molecular electric dipole moments [1–3]. Actually both, the quadrupole moments and the dipole moments are not obtained directly from the Zeeman spectra, but are calculated from the measured diagonal elements of the molecular g-tensor, from the anisotropies of the magnetic susceptibility tensor, and from the rotational constants by use of the theoretical expressions for these molecular parameters. Since the theoretical expressions were only derived within the rigid rotor model [4–6], the vast majority of molecules whose rotational Zeeman effect has been studied so far are molecules with a sufficiently deep and sharp potential well at the equilibrium configuration, so as to make the rigid nuclear frame model a fairly good approximation to the real molecule — at least as fast as rotational spectroscopy is concerned.

One prominent class of molecules for which the rigid rotor approximation fails are molecules showing low barrier internal rotations [7, 8]. In such molecules an additional magnetic moment, associated with the internal rotation, has to be accounted for. This effect is most pronounced in molecules with low barrier methyl top internal rotation, since the rotational electric currents associated with a given internal angular momentum of the light methyl top lead to comparatively big magnetic moments. These are typically on the order of one nuclear magneton, i.e. more than one order of magnitude larger than those associated with the overall rotation of the molecule. Nitromethane, CH_3NO_2, and Methylbortrifluoride, CH_3BF_2, may serve as examples.

In the following we present a derivation of the effective Zeeman rotorsional Hamiltonian for molecules with low barrier methyl top internal rotation. The derivation leads to theoretical expressions for the g- and χ-tensor elements etc. and it makes it possible to extract the molecular electric quadrupole moments etc. from the Zeeman data also for this class of molecules.

Since the Hamiltonian, including electronic motion, has essentially been derived in an earlier publication [9], we will only briefly sketch its derivation in the first section. The main emphasis of the present paper will be on the perturbation treatment within the electronic states which leads to the "effective rotorsional Hamiltonian" and to the theoretical expressions for the g-tensor elements and other molecular parameters determined by microwave spectroscopy. Since $\mathscr{P}_\alpha$, the operator corresponding to the torsional angular momentum, also acts on the electronic wavefunctions, the perturbation treatment is slightly more complicated

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than in the rigid rotor case. In the final section we will also present a detailed discussion of the symmetry properties of the molecular parameters with respect to internal rotation. As most low barrier molecules investigated so far do possess a molecular frame with C_{2v} symmetry, the equations will be specialized to this case.

II. Derivation of the Hamiltonian within the Rigid Top/Rigid Frame Model

Our derivation of the Hamiltonian closely follows the line of thought already used in the case of rigid rotor molecules [10].

Starting point is the classical Lagrangian for an ensemble of charged particles in an exterior magnetic field.

Within this classical Lagrangian we neglect all intramolecular magnetic interactions as compared to the magnetic interactions with the strong exterior field. (Their inclusion would lead to the expressions for the spin-rotation coupling tensor and for the nuclear shielding tensor which in most cases are only of minor importance for the study of rotational Zeeman-effect splittings.) With these neglections the classical Lagrangian takes the form given in Equation (1) [11].

$$\mathscr{L} = \sum_{\nu}^{\text{nuclei}} \frac{m_\nu}{2} \boldsymbol{V}_\nu^2 + \sum_{\varepsilon}^{\text{electrons}} \frac{m}{2} \boldsymbol{V}_\varepsilon^2 - V_{\text{Coulomb}} + \frac{e}{c} \sum_{\nu}^{\text{nuclei}} Z_\nu \boldsymbol{V}_\nu \cdot \boldsymbol{A}_\nu - \frac{e}{c} \sum_{\varepsilon}^{\text{electrons}} \boldsymbol{V}_\varepsilon \cdot \boldsymbol{A}_\varepsilon , \quad (1)$$

m_ν = mass of ν-th nucleus, m = electron mass;

$\boldsymbol{V}_\nu$ = velocity of ν-th nucleus,
$\boldsymbol{V}_\varepsilon$ = velocity of ε-th electron,
} with respect to the laboratory frame;

$$V_{\text{Coulomb}} = -\sum_{\nu}^{\text{nuclei}} \sum_{\varepsilon}^{\text{electrons}} \frac{Z_\nu e^2}{|\boldsymbol{R}_\nu - \boldsymbol{R}_\varepsilon|} + \frac{e^2}{2} \sum_{\substack{\varepsilon \\ \varepsilon' \neq \varepsilon}}^{\text{electrons}} \sum_{\varepsilon'} \frac{1}{|\boldsymbol{R}_\varepsilon - \boldsymbol{R}_{\varepsilon'}|} + \frac{e^2}{2} \sum_{\substack{\nu \\ \nu \neq \nu'}}^{\text{nuclei}} \sum_{\nu'} \frac{Z_\nu Z_{\nu'}}{|\boldsymbol{R}_\nu - \boldsymbol{R}_{\nu'}|}$$

= Coulomb potential energy of the molecular charge distribution,

Z_ν = atomic number of ν-th nucleus,

e = elementary charge (proton charge),

$\boldsymbol{R}_\nu, \boldsymbol{R}_\varepsilon$ = vectors pointing from the origin of the laboratory frame to the positions of the ν-th nucleus and ε-th electron, respectively,

$\boldsymbol{A}_\nu = [\boldsymbol{H} \times \boldsymbol{R}_\nu]/2$ = vectorpotential associated with the exterior field, $\boldsymbol{H}$, at the position of the ν-th nucleus,

$\boldsymbol{A}_\varepsilon = [\boldsymbol{H} \times \boldsymbol{R}_\varepsilon]/2$ = vectorpotential of the exterior field at the position of the ε-th electron,

c = velocity of light.

In the second step we introduce the rigid top rigid frame approximation together with a molecular coordinate system attached to the nuclear frame now assumed to be rigid. In other words: we describe the molecular system using a reduced number of variables, i.e. generalized coordinates, which implicitly account for the constraints imposed on the nuclear motion by the rigid top/rigid frame model. Equation (1) is then rewritten using these generalized coordinates, q_k, and we obtain the classical Hamiltonian as

$$\mathscr{H} = \sum_k p_k \dot{q}_k - \mathscr{L} = \sum_{i,k} p_i g^{ik} p_k + V(q_k) \quad (2)$$

with $p_k = \partial \mathscr{L} / \partial \dot{q}_k$ the momenta conjugated to the generalized coordinates q_k.

In Eq. (2) the coefficients g^{ik} which enter into the expression for the kinetic energy may depend on the generalized coordinates. $V(q_k)$ stands for the potential energy.

In the final step we perform the translation to quantum mechanics by replacing the momenta, p_k, by the corresponding differential operators

$$\hat{p}_k \triangleq \frac{\hbar}{i} \frac{\partial}{\partial q_k}$$

while Eq. (2) is rearranged as given in Equation (3) [12].

$$\mathscr{H} = g^{1/4} \sum_{i,k} p_i \frac{g^{ik}}{\sqrt{g}} p_k g^{1/4} + V(q_k); \quad g = \text{Det}(g^{ik}) . \quad (3)$$

Although it has been shown that the above described procedure of introducing constraints may lead to results which differ from those which would be obtained from the complete Hamiltonian when going to the limit of infinitely sharp and deep potential wells corresponding to the constraints introduced by the model [13], we believe that, as

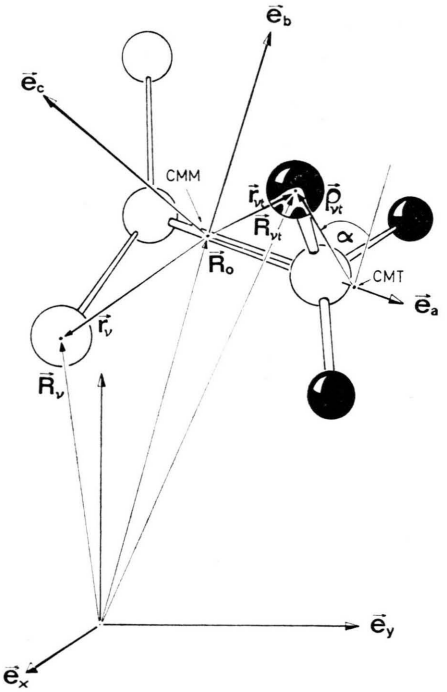

Fig. 1. Nitromethane, CH_3NO_2, is used to illustrate the model upon which the derivation of the Hamiltonian is based. The nuclear frame (light atoms and bond sticks) and the top (black atoms and bond sticks) both are assumed to be rigid, leaving the internal rotation about the N-C bond axis the only internal degree of freedom for the nuclear system. Also depicted are the nuclear principal inertia axes e_a, e_b and e_c, which serve as molecular reference system and whose orientation with respect to the space laboratory system e_x, e_y and e_z are described by the Eulerian angles (not shown). R_0 = vector pointing from the origin of the laboratory frame to the nuclear center of mass; capital letters denote position vectors with reference to the laboratory frame, small letters denote position vectors with respect to the molecular frame (CMM = center of mass of the nuclear configuration of the molecule; CMT = center of mass of the nuclear configuration of the top).

far as rotational spectroscopy is concerned, the results obtained from the so derived Hamiltonian will be correct.

As molecular coordinate system we choose the principal interia axes system of the nuclear frame (see Figure 1). Following the standard notation the unit vector pointing into the direction of the axis of least moment of intertia is designated by e_a the unit vector pointing into the direction of the axis of greatest moment of intertia is designated by e_c. If the symmetry axis of the top (which is assumed to have at least C_{3v} symmetry) coincides with its internal rotation axis, as we will assume throughout this paper, the orientation of the so defined molecular coordinates system does not depend on the internal rotation angle α. Quite in general however, due to the overall rotation of the molecules, the molecular axes will change their orientation with time and the time derivatives of the basis vectors e_a, e_b and e_c may be written as:

$$\mathrm{d}e_\gamma/\mathrm{d}t = \boldsymbol{\omega} \times e_\gamma\,, \quad \gamma = a, b, c\,, \tag{4}$$

where

$$\boldsymbol{\omega} = \sum_\gamma \omega_\gamma\, e_\gamma$$

is the instantaneous angular velocity associated with the overall rotation.

The transformation to generalized coordinates is now performed by using the coordinates of the nuclear center of mass and coordinates with respect to the nuclear principal axes system to rewrite Equation (1).

For the position vectors we have (see Figure 1):

i) electrons:

$$\boldsymbol{R}_\varepsilon = \underbrace{x_0\, e_x + y_0\, e_y + z_0\, e_z}_{\boldsymbol{R}_0} + \underbrace{a_\varepsilon\, e_a + b_\varepsilon\, e_b + c_\varepsilon\, e_c}_{\boldsymbol{r}_\varepsilon} \tag{5}$$

ii) nuclei:

$$\boldsymbol{R}_\nu = \boldsymbol{R}_0 + \boldsymbol{r}_\nu\,. \tag{6}$$

For the velocities we get:

i) electrons:

$$\begin{aligned}\mathrm{d}\boldsymbol{R}_\varepsilon/\mathrm{d}t = {} & \dot{x}_0\, e_x + \dot{y}_0\, e_y + \dot{z}_0\, e_z + \dot{a}_\varepsilon\, e_a + \dot{b}_\varepsilon\, e_b + \dot{c}_\varepsilon\, e_c \\ = {} & \boldsymbol{V}_0 + \boldsymbol{v}_\varepsilon \\ & + a_\varepsilon\, \dot{e}_a + b_\varepsilon\, \dot{e}_b + c_\varepsilon\, \dot{e}_c \\ & + \boldsymbol{\omega} \times \boldsymbol{r}_\varepsilon \end{aligned} \tag{7}$$

($\boldsymbol{v}_\varepsilon$ = velocity of ε-th electron relative to the rigid nuclear frame);

ii) nuclei of the frame:

$$\mathrm{d}\boldsymbol{R}_\nu/\mathrm{d}t = \boldsymbol{V}_0 + \boldsymbol{\omega} \times \boldsymbol{r}_\nu; \tag{8}$$

iii) nuclei of the top:

$$\mathrm{d}\boldsymbol{R}_{\nu_t}/\mathrm{d}t = \boldsymbol{V}_0 + \boldsymbol{\omega} \times \boldsymbol{r}_{\nu_t} + \dot{\alpha}(\boldsymbol{\Lambda} \times \boldsymbol{\rho}_{\nu_t})\,. \tag{9}$$

In Eq. (9) $\boldsymbol{\Lambda}$ is the unit vector pointing into the direction of the internal rotation axis and $\boldsymbol{\rho}_{\nu_t}$ is the vector pointing from the center of mass of the top to the ν_t-th nucleus of the top (in Fig. 1 the vector $\boldsymbol{\Lambda}$ coincides with e_a). Insertion of Eqs. (5) through (9) into Eq. (1) leads to the Lagrangian as expressed by the electron coordinates and -velocities γ_ε, $\dot{\gamma}_\varepsilon$ ($\gamma = a, b, c$), by the angular velocities, ω_γ, and by

the X-, Y-, and Z-components of the velocity of the nuclear center of mass, $\dot{X}_0, \dot{Y}_0, \dot{Z}_0$ (actually the orientational dependence of the Lagrangian should be expressed by using the Eulerian angles and their time derivatives, but it may be shown, that the use of the ω_γ also leads to the correct result [14]). The $\boldsymbol{R}_0$-dependence, formally present in the vector potential of the exterior magnetic field, may be eliminated by a suitable gauge transformation [15—17]. From the so derived Lagrangian for the rigid frame-rigid top model, the routine procedure sketched above leads to the final Hamiltonian which after the neglection of contributions that are small on the order of (m/M) (M = molecular mass) [18] takes the following form:

$$\mathscr{H} = \frac{1}{2m} \sum_{\varepsilon}^{\text{electrons}} [p_{a\varepsilon}^2 + p_{b\varepsilon}^2 + p_{c\varepsilon}^2]^* + V_{\text{Coulomb}} \tag{10a}$$

$$+ \tfrac{1}{2}[P_a - l_a, P_b - l_b, P_c - l_c, P_\alpha] \cdot \begin{pmatrix} \frac{1}{I_{aa} - I_\alpha} & 0 & 0 & -\frac{1}{(I_{aa} - I_\alpha)} \\ 0 & \frac{1}{I_{bb}} & 0 & 0 \\ 0 & 0 & \frac{1}{I_{cc}} & 0 \\ -\frac{1}{I_{aa} - I_\alpha} & 0 & 0 & \frac{1}{I_\alpha(1 - I_\alpha/I_{aa})} \end{pmatrix} \cdot \begin{bmatrix} P_a - l_a \\ P_b - l_b \\ P_c - l_c \\ P_\alpha \end{bmatrix} \tag{10b}$$

$$- \frac{e}{4c} H_z [\cos a Z, \cos b Z, \cos c Z] \cdot \tag{10c'}$$

$$\cdot \begin{pmatrix} \frac{\sum_\nu^{\text{nuclei}} Z_\nu(b_\nu^2 + c_\nu^2) - 3Z_t r_t^2}{I_{aa} - I_\alpha} & 0 & 0 & \left[-\frac{\sum_\nu^{\text{nuclei}} Z_\nu(b_\nu^2 + c_\nu^2)}{I_{aa} - I_\alpha} + \frac{3Z_t r_t^2}{I_\alpha} \right] \\ 0 & \frac{\sum_\nu^{\text{nuclei}} Z_\nu(b_\nu^2 + c_\nu^2)}{I_{bb}} & 0 & 0 \\ 0 & 0 & \frac{\sum_\nu^{\text{nuclei}} Z_\nu(a_\nu^2 + b_\nu^2)}{I_{cc}} & 0 \end{pmatrix} \cdot \begin{bmatrix} P_a - l_a \\ P_b - l_b \\ P_a - l_c \\ P_\alpha \end{bmatrix}$$

$$- \frac{e}{4c} H_z [P_a - l_a, P_b - l_b, P_a - l_c, P_\alpha] \tag{10c''}$$

$$\cdot \begin{pmatrix} \frac{\sum_\nu^{\text{nuclei}} Z_\nu(b_\nu^2 + c_\nu^2) - 3Z_t r_t^2}{I_{aa} - I_\alpha} & 0 & 0 \\ 0 & \frac{\sum_\nu^{\text{nuclei}} Z_\nu(c_\nu^2 + a_\nu^2)}{I_{bb}} & 0 \\ 0 & 0 & \frac{\sum_\nu^{\text{nuclei}} Z_\nu(a_\nu^2 + b_\nu^2)}{I_{cc}} \\ \left[-\frac{\sum_\nu^{\text{nuclei}} Z_\nu(b_\nu^2 + c_\nu^2) - 3Z_t r_t^2}{I_{aa} - I_\alpha} + \frac{3Z_t r_t^2}{I_\alpha} \right] & 0 & 0 \end{pmatrix} \cdot \begin{bmatrix} \cos a Z \\ \cos b Z \\ \cos c Z \end{bmatrix}$$

$$+ \frac{e H_z}{2mc} [l_a, l_b, l_c] \cdot \begin{bmatrix} \cos a Z \\ \cos b Z \\ \cos c Z \end{bmatrix} \tag{10d}$$

* All expressions in the boldface brackets [ ] are operators as $\mathscr{H}$, $\mathscr{P}$, and $\mathscr{S}$.

$$+\frac{e^2}{8mc^2}H_z^2\,[\cos a\,Z,\cos b\,Z,\cos c\,Z]\cdot\begin{bmatrix}\sum\limits_{\varepsilon}^{\text{electrons}}(b_\varepsilon^2+c_\varepsilon^2) & -\sum\limits_{\varepsilon}^{\text{electrons}}a_\varepsilon b_\varepsilon & -\sum\limits_{\varepsilon}^{\text{electrons}}a_\varepsilon c_\varepsilon\\ -\sum\limits_{\varepsilon}^{\text{electrons}}b_\varepsilon a_\varepsilon & \sum\limits_{\varepsilon}^{\text{electrons}}(c_\varepsilon^2+a_\varepsilon^2) & -\sum\limits_{\varepsilon}^{\text{electrons}}b_\varepsilon c_\varepsilon\\ -\sum\limits_{\varepsilon}^{\text{electrons}}c_\varepsilon a_\varepsilon & -\sum\limits_{\varepsilon}^{\text{electrons}}c_\varepsilon b_\varepsilon & \sum\limits_{\varepsilon}^{\text{electrons}}(a_\varepsilon^2+b_\varepsilon^2)\end{bmatrix}\cdot\begin{bmatrix}\cos a\,Z\\ \cos b\,Z\\ \cos c\,Z\end{bmatrix} \tag{10e}$$

$$-\frac{1}{c}\,[\mu_a,\mu_b,\mu_c]\cdot\begin{bmatrix}\cos a\,X & \cos a\,Y & \cos a\,Z\\ \cos b\,X & \cos b\,Y & \cos b\,Z\\ \cos c\,X & \cos c\,Y & \cos c\,Z\end{bmatrix}\cdot\begin{bmatrix}V_{0y}H_z\\ -V_{0x}H_z\\ 0\end{bmatrix}. \tag{10f}$$

In Eq. (10) the Hamiltonian is written in matrix notation with the heavy dot indicating the matrix-multiplication. The Hamiltonian is already arranged for direct translation into quantum mechanics i.e. it is written in a form equivalent to Equation (3). Unless defined previously the symbols have the following meanings:

$p_{\gamma\varepsilon}=\dfrac{\partial\mathscr{L}}{\partial\dot{\gamma}_\varepsilon}$ $(\gamma_\varepsilon=a_\varepsilon,b_\varepsilon,c_\varepsilon)$ linear momentum of the ε-th electron in direction of $\boldsymbol{e}_\gamma$ $(\gamma=a,b,c)$,

$P_\gamma=\dfrac{\partial\mathscr{L}}{\partial\omega_\gamma}$ components of the overall angular momentum (see also Ref. [14]).

$l_\gamma=\sum\limits_{\varepsilon}^{\text{electrons}}(\gamma_\varepsilon' p_{\gamma\varepsilon}''-\gamma_\varepsilon'' p_{\gamma'\varepsilon})$ $(\gamma,\gamma',\gamma''$ in cyclic permutation) components of the electronic angular momentum.

$I_{\gamma\gamma}=\sum\limits_{\nu}^{\text{nuclei}}m_\nu(\gamma_\nu'^2+\gamma_\nu''^2)$ $(\gamma,\gamma',\gamma''$ in cyclic permutation) principal inertia moments of the nuclear configuration.

$I_\alpha=\sum\limits_{\nu_t}^{\text{nuclei of the top}}m_{\nu_t}\boldsymbol{\rho}_{\nu_t}^2$ nuclear moment of inertia of the top about its internal rotation axis (see Figure 1),

Z_t atomic number of the nuclei of the top (all assumed to be equal),

$r_t=|\boldsymbol{\rho}_{\nu_t}|$ radial distance of the nuclei of the top from the axis of internal rotation,

$\mu_\gamma=e\left(\sum\limits_{\nu}^{\text{nuclei}}Z_\nu\gamma_\nu-\sum\limits_{\varepsilon}^{\text{electrons}}\gamma_\varepsilon\right)$ components of the molecular electric dipole moment.

As compared to the Hamiltonian derived earlier [19] we have assumed C_{2v} symmetry of the nuclear frame with the twofold axis coinciding with the internal rotation axis and pointing in the direction of the a-principal inertia axis. This simply reduces some off diagonal elements in the matrices to zero and makes the results directly applicable to most low barrier molecules investigated so far. Furthermore no distinction is made between electrons associated with the top and electrons associated with the frame. All electrons are referred to the frame. The translational Zeeman effect [20] (10f), $-\boldsymbol{\mu}\cdot(\boldsymbol{V}_0\times\boldsymbol{H})/c$, has also been included. It is of considerable importance for E-species rotational transitions, quite similar to the situation encountered for symmetric top molecules [21]. The exterior field is assumed to point into the Z-direction.

III. Derivation of the Effective Rotorsional Hamiltonian by a Second Order Perturbation within the Electronic States

Since the spacing of the electronic energy levels is large as compared to that of the torsional levels and even more to that of the rotational levels, it is in general not necessary to use the full Hamiltonian as given in Eq. (10), if one is interested in the analysis of rotational spectra. Instead, a second order perturbation treatment within the electronic states, i.e. a Van Vleck transformation [22, 23] will usually lead to an effective torsio-rotational Hamiltonian which corresponds to Eq. (10) with a sufficient degree of accuracy as long as only rotational spectroscopy is concerned. In this effective Hamiltonian only four degrees of freedom are retained, three for the overall rotation and one for the internal rotation of the top. The special electronic state under consideration — in our case the electronic ground state — enters implicity via a number of molecular parameters such as for instance the elements of the g-tensor and of the

susceptibility tensor whose theoretical expressions include electronic ground state expectation values and (or) electronic perturbation sums and whose numerical values may be determined experimentally by a fit to the observed spectra.

Before entering into the perturbation treatment we will first write down the expected structure of the effective Hamiltonian as it may be anticipated from rather general physical arguments. This effective Hamiltonian should include expressions for:

a) the kinetic energy;

b) the internal potential energy corresponding to the barrier of internal rotation, i.e. $V(\alpha)$;

c) the orientational energy due to the rotational magnetic moments (g-tensor contribution or "first order" Zeeman effect);

d) the orientational energy due to the field induced magnetic moment (χ-tensor contribution or "second order" Zeeman effect),

and

e) the orientational energy corresponding to the Lorentz forces on the molecular dipole moment (translational Zeeman effect).

For the kinetic energy (a) we expect a quadratic form in the four angular momenta $\mathscr{P}_a = \hbar \mathscr{J}_a$, $\mathscr{P}_b = \hbar \mathscr{J}_b$, $\mathscr{P}_c = \hbar \mathscr{J}_c$ and $\mathscr{P}_\alpha = \hbar \mathscr{J}_\alpha$.

Thus we expect an expression of the form given in Eq. (11a) with a generalized four by four "rotational constants matrix" rather than the standard three by three matrix encountered in the rigid rotor case. For the orientational energy of the rotational magnetic moment we expect an expression as given in Eq. (11c) where a three by four g-matrix accounts for the fact that, depending on the special geometry of the molecule, the rotational a-, b- and c-magnetic moments may include contributions due to all four angular momenta i.e. to $\mathscr{J}_a$, $\mathscr{J}_b$, $\mathscr{J}_c$ and $\mathscr{J}_\alpha$. In order to make this Zeeman effect contribution Hermitian, we expect it to be split into two parts given in Eqs. (11c') and (11c'').

For the field induced "second order" Zeeman effect (11d) and the translational Zeeman effect (11e) there is no reason to expect a form different from the one already encountered in the case of rigid motor molecules. Quite general however the matrix elements of the G-, g- and χ-matrices as well as those for the electric dipole moment entering into Eq. (11) may depend on the internal rotation angle α. We will discuss the general features of this α-dependence later in Sect. IV of this paper.

$$\mathscr{H}_{\text{eff}} = [J_a, J_b, J_c, J_\alpha] \cdot \begin{pmatrix} G_{aa} & G_{ab} & G_{ac} & G_{a\alpha} \\ G_{ab}^* & G_{bb} & G_{bc} & G_{b\alpha} \\ G_{ac}^* & G_{bc}^* & G_{cc} & G_{c\alpha} \\ G_{a\alpha}^* & G_{b\alpha}^* & G_{c\alpha}^* & G_{cc} \end{pmatrix} \cdot \begin{bmatrix} J_a \\ J_b \\ J_c \\ J_\alpha \end{bmatrix} \tag{11a}$$

$$+ \mathscr{V}(\alpha) \tag{11b}$$

$$- \frac{\mu_N}{2} H_z [\cos a\, Z, \cos b\, Z, \cos c\, Z] \cdot \begin{pmatrix} g_{aa} & g_{ab} & g_{ac} & g_{a\alpha} \\ g_{ba} & g_{bb} & g_{bc} & g_{b\alpha} \\ g_{ca} & g_{cb} & g_{cc} & g_{c\alpha} \end{pmatrix} \cdot \begin{bmatrix} J_a \\ J_b \\ J_c \\ J_\alpha \end{bmatrix} \tag{11c'}$$

$$- \frac{\mu_N}{2} H_z [J_a, J_b, J_c, J_\alpha] \cdot \begin{pmatrix} g_{aa}^* & g_{ba}^* & g_{ca}^* \\ g_{ab}^* & g_{bb}^* & g_{cb}^* \\ g_{ac}^* & g_{bc}^* & g_{cc}^* \\ g_{a\alpha}^* & g_{b\alpha}^* & g_{c\alpha}^* \end{pmatrix} \cdot \begin{bmatrix} \cos a\, Z \\ \cos b\, Z \\ \cos c\, Z \end{bmatrix} \tag{11c''}$$

$$- \tfrac{1}{2} H_z^2 [\cos a\, Z, \cos b\, Z, \cos c\, Z] \cdot \begin{pmatrix} \chi_{aa} & \chi_{ab} & \chi_{ac} \\ \chi_{ab}^* & \chi_{bb} & \chi_{bc} \\ \chi_{ac}^* & \chi_{bc}^* & \chi_{cc} \end{pmatrix} \cdot \begin{bmatrix} \cos a\, Z \\ \cos b\, Z \\ \cos c\, Z \end{bmatrix} \tag{11d}$$

$$- \frac{1}{c} \mu_a^{eff} \cdot H_z [\cos a\, X V_{0y} - \cos a\, Y V_{0x}] \tag{11e}$$

with $\mu_N = e\hbar/2 m_p c$ = nuclear magneton.

In Eq. (11) complex conjugate quantities are indicated by an asterisk. μ_a^{eff} is the effective molecular electric dipole moment (ground state expectation value). V_0 with y- and z-components V_{0y} and V_{0z}, the translational velocity of the molecule, will be treated classically.

We will now show that the formulas obtained from a Van Vleck transformation aiming at the electronic ground state may indeed be cast into a form as given by Equation (11).

To this end we will first define the wavefunctions which we intend to use as a basis to set up the Hamiltonian matrix corresponding to Equation (10).

We first assume that the solutions of the electronic Schrödinger-Equation ("infinite nuclear mass approximation") Eq. (10a) are known for each value of α (at least in principle). We write them as:

$$\varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots) \quad \text{i.e.:}$$
$$\mathscr{H}_{\text{el}}\, \varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots) = E_n(\alpha)\, \varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots) \tag{12}$$

with

$$\mathscr{H}_{\text{el}} = -\frac{\hbar^2}{2m} \sum_{\varepsilon}^{\text{electrons}} \left(\frac{\partial^2}{\partial a_\varepsilon^2} + \frac{\partial^2}{\partial b_\varepsilon^2} + \frac{\partial^2}{\partial c_\varepsilon^2} \right)$$
$$- \sum_{\nu}^{\substack{\text{nuclei of} \\ \text{the frame}}} \sum_{\varepsilon}^{\text{electrons}} \frac{Z_\nu e^2}{|\boldsymbol{r}_\varepsilon - \boldsymbol{r}_\nu|} + \tfrac{1}{2} \sum_{\varepsilon}^{\text{electrons}} \sum_{\substack{\varepsilon' \\ \varepsilon \neq \varepsilon'}}^{\text{electrons}} \frac{e^2}{|\boldsymbol{r}_\varepsilon - \boldsymbol{r}_{\varepsilon'}|} + V_{\text{Coul, nucl}}(\alpha) \tag{13}$$
$$- \sum_{\varepsilon}^{\text{electrons}} \left[\frac{Z_t e^2}{((a_\varepsilon - a_{\text{I}})^2 + (b_\varepsilon - b_{\text{I}})^2 + (c_\varepsilon - c_{\text{I}})^2)^{1/2}} + \frac{Z_t e^2}{((a_\varepsilon - a_{\text{II}})^2 + (b_\varepsilon - b_{\text{II}})^2 + (c_\varepsilon - c_{\text{II}}))^{1/2}} \right.$$
$$\left. + \frac{Z_t e^2}{((a_\varepsilon - a_{\text{III}})^2 + (b_\varepsilon - b_{\text{III}})^2 + (c_\varepsilon - c_{\text{III}})^2)^{1/2}} \right].$$

$a_{\text{I}}, b_{\text{I}}, c_{\text{I}}, a_{\text{II}}, b_{\text{II}}, c_{\text{II}}, a_{\text{III}}, b_{\text{III}}, c_{\text{III}}$ = coordinates of the nuclei of the top (assumed to be set up by three nuclei only).

$V_{\text{Coul, nucl}}(\alpha)$ = Coulomb repulsion energy of the nuclear configuration.

In accordance to our basic assumption that we are dealing only with low barrier molecules, the α-dependence of the electronic eigenvalues may be assumed to be weak and we split them into a constant, E_n, and a small α-dependent term, $\varepsilon_n(\alpha)$. As E_n we define the average eigenvalue averaged over one full revolution of the top:

$$E_n = \frac{1}{2\pi} \int_0^{2\pi} E_n(\alpha)\, \mathrm{d}\alpha\,.$$

We now assume the Hamiltonian matrix to be set up within a set of basis functions constructed from products of the electronic wavefunctions, φ_n, depending on the electronic coordinates and — "parametrically" — on the internal rotation angle α; of symmetric top wavefunctions, $\psi_{JKM}(\Theta, \Phi, \chi)$, depending on the Eulerian angles Θ, Φ, χ and of the eigenfunctions of the free internal rotor $e^{im\alpha}/\sqrt{2\pi}$ (m integer). To avoid too clumsy writing, we reduce the number of subscripts used to characterize the basisfunctions to two; one, n, to indicate the electronic wavefunctions, and a second, j, to indicate the rotorsional wavefunctions, and we introduce the following shorthand notation:

$$|n\rangle\,|j\rangle = \underbrace{\varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)}_{|n\rangle} \cdot \underbrace{\psi_{JKM}(\Theta, \Phi, \chi) \cdot e^{im\alpha}/\sqrt{2\pi}}_{|j\rangle}\,. \tag{14}$$

We assume the corresponding Hamiltonian matrix to be broken up into a sum of two matrices resulting from a zeroth order Hamiltonian, $\mathscr{H}_0$, and a perturbation, $\mathscr{S}$:

$$\langle j|\langle n|\mathscr{H}|n'\rangle|j'\rangle = \langle j|\langle n|\mathscr{H}_0|n'\rangle|j'\rangle + \langle j|\langle n|\mathscr{S}|n'\rangle|j'\rangle\,.$$

As zeroth order Hamiltonian we essentially take the electronic Hamiltonian but we eliminate all α-dependence from its eigenvalues by defining

$$\mathscr{H}_0 = \mathscr{H}_{\text{el}} - \sum_n \varepsilon_n(\alpha)\, \mathscr{P}_n \tag{15}$$

where $\mathscr{P}_n$ stands for the projection operator defined by:

$$\delta_{nn'}\, \varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots) = \mathscr{P}_n\, \varphi_{n'}(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)\,. \tag{16}$$

This simplifies the further discussion (the electronic eigenfunctions are the same for $\mathscr{H}_0$ and $\mathscr{H}_{\text{el}}$.) The perturbation operator $\mathscr{S}$ stands for the contributions given by Eqs. (10b) through (10f) plus

$$\sum_n^{\substack{\text{electronic} \\ \text{states}}} \varepsilon_n(\alpha)\, \mathscr{P}_n\,.$$

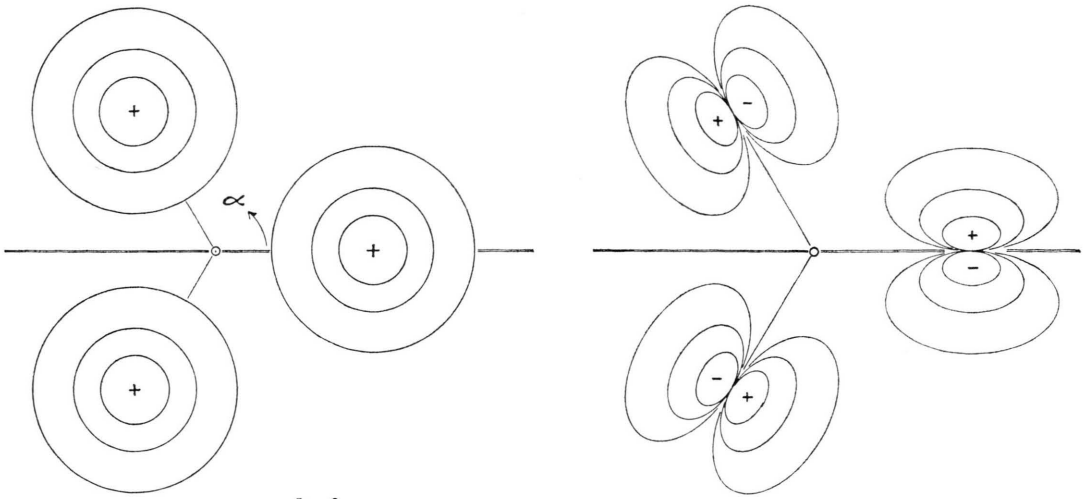

Fig. 2. The effect of $P_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial\alpha}$ on a special molecular orbital of Nitromethane is shown in this Figure (the projection is along the C-N-bond). On the left hand side a molecular orbital which includes three Hydrogen-1s-atomic orbitals with approximately equal weight is depicted schematically. The right hand drawing shows the result of application of P_α on this orbital. For clearty the contributions from atomic orbitals centered at the C, N, and O atoms are not shown. Within the CNDO-approximation this part of the molecular orbitals remains essentially unchanged upon internal rotation i.e. application of P_α essentially leads to zero in the frame region.

If we now retain only the leading terms of the Van Vleck expansion, the matrix elements of the effective rotorsional Hamiltonian take the following form:

$$\langle j|\mathscr{H}_{\text{eff}}|j'\rangle = E_0\,\delta_{jj'} + \langle j|\langle 0|\mathscr{S}|0\rangle|j'\rangle + \sum_{n''}\sum_{j''}\frac{\langle j|\langle 0|\mathscr{S}|n''\rangle|j''\rangle\langle j''|\langle n''|\mathscr{S}|0\rangle|j'\rangle}{E_0 - E_{n''}}. \quad (17)$$

(We write $\langle j|\langle 0|\mathscr{S}|n''\rangle|j''\rangle$ rather than $\langle j, 0|\mathscr{S}|j'', n''\rangle$ etc.

in order to emphasize that, due to the α-dependence of the electronic wavefunctions, the integration over the electron coordinates has to be carried out prior to the integration over the torsional angle α.)

As is indicated by writing the left hand side of Eq. (17) as $\langle j|\mathscr{H}_{\text{eff}}|j'\rangle$, the theoretical expressions for the G-, g- and χ-matrix elements of the effective Hamiltonian, Eq. (11) are contained in the right hand side of Equation (17).

At first sight, due to the rather complicated structure of the operator $\mathscr{S}$, the great number of different perturbation contributions arising at the right hand side may appear prohibitive, but order of magnitude considerations and symmetry arguments may be used to largely reduce their number. Since these considerations are essentially the same as in the rigid rotor case, we will not repeat them here. The reader is referred to Chapt. IV, p. 173 in Ref. [3].

However, due to the fact that $\mathscr{P}_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial\alpha}$ operates on both, the torsional functions $e^{im\alpha}/\sqrt{2\pi}$ *and* the parametrically α-dependent electronic wavefunctions $\varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)$ (see Fig. 2) the extraction of the G-, g- and χ-matrix elements from the right hand side of Eq. (17) is not quite as straightforward as in the rigid rotor case. Rather the right hand side needs some rearrangements and manipulations before it can be compared directly to Equation (11).

In order to save printing space we will describe the essential features of the perturbation treatment and the necessary subsequent manipulations by considering only the following part of the complete Hamiltonian:

$$\mathscr{H}_{\text{p}} = \mathscr{H}_0 + \sum_n \varepsilon_n(\alpha)\,\mathscr{P}_n + \tfrac{1}{2}[P_a - l_a, P_\alpha] \cdot \begin{pmatrix} \frac{1}{(I_{aa} - I_\alpha)} & -\frac{1}{(I_{aa} - I_\alpha)} \\ -\frac{1}{(I_{aa} - I_\alpha)} & \frac{1}{I_\alpha(1 - I_\alpha/I_{aa})} \end{pmatrix} \cdot \begin{bmatrix} P_a - l_a \\ P_\alpha \end{bmatrix} + \frac{e}{2mc} H_z\,[l_a \cos a\,Z]\,. \quad (18)$$

$\mathscr{H}_{\text{p}} = \mathscr{H}_0 + \mathscr{S}_{\text{p}}$ includes the complete electronic Hamiltonian (10a) as well as parts of (10b) and (10d).

Table 1. Theoretical expressions for the "rotational constants" (see Equation (11a)).

$$G_{aa} = \frac{h}{8\pi^2(I_{aa} - I_\alpha)} + \frac{h}{4\pi^2(I_{aa} - I_\alpha)^2} \cdot \sum_n \frac{\langle 0|\, l_a + P_\alpha^{(n)} \,|n\rangle|^2}{E_0 - E_n}$$

$$G_{ab} = \frac{h}{4\pi^2(I_{aa} - I_\alpha)\, I_{bb}} \cdot \sum_n \frac{\langle 0|\, l_a + P_\alpha^{(n)} \,|n\rangle\langle n|\, l_b \,|0\rangle}{E_0 - E_n}$$

$$G_{ac} = + \frac{h}{4\pi^2(I_{aa} - I_\alpha)\, I_{cc}} \cdot \sum_n \frac{\langle 0|\, l_a + P_\alpha^{(n)} \,|n\rangle\langle n|\, l_a \,|0\rangle}{E_0 - E_n}$$

$$G_{a\alpha} = -\frac{h}{8\pi^2(I_{aa} - I_\alpha)} - \frac{h}{4\pi^2(I_{aa} - I_\alpha)^2} \cdot \sum_n \frac{|\langle 0|\, l_a + P_\alpha^{(n)} \,|n\rangle|^2}{E_0 - E_n} - \frac{h}{4\pi^2\, I_\alpha(I_{aa} - I_\alpha)} \cdot \sum_n \frac{\langle 0|\, l_a + P_\alpha^{(n)} \,|n\rangle\langle n|\, P_\alpha^{(n)} \,|0\rangle}{E_0 - E_n}$$

$$G_{bb} = \frac{h}{8\pi^2\, I_{bb}} + \frac{h}{4\pi^2\, I_{bb}^2} \sum_n \frac{|\langle 0|\, l_b \,|n\rangle|^2}{E_0 - E_n}$$

$$G_{bc} = + \frac{h}{4\pi^2\, I_{bb}\, I_{cc}} \cdot \sum_n \frac{\langle 0|\, l_b \,|n\rangle\langle n|\, l_c \,|0\rangle}{E_0 - E_n}$$

$$G_{b\alpha} = -\frac{h}{4\pi^2\, I_{bb}\, I_\alpha} \sum_n \frac{\langle 0|\, l_b \,|n\rangle\langle n|\, P_\alpha^{(n)} \,|0\rangle}{E_0 - E_n} - \frac{h}{4\pi^2\, I_{bb}(I_{aa} - I_\alpha)} \cdot \sum_n \frac{\langle 0|\, l_b \,|n\rangle\langle n|\, l_a + P_\alpha^{(n)} \,|0\rangle}{E_0 - E_n}$$

$$G_{cc} = \frac{h}{8\pi^2\, I_{cc}} + \frac{h}{4\pi^2\, I_{cc}^2} \sum_n \frac{|\langle 0|\, l_c \,|n\rangle|^2}{E_0 - E_n}$$

$$G_{c\alpha} = -\frac{h}{4\pi^2\, I_{cc}\, I_\alpha} \sum_n \frac{\langle 0|\, l_c \,|n\rangle\langle n|\, P_\alpha^{(n)} \,|0\rangle}{E_0 - E_n} - \frac{h}{4\pi^2\, I_\alpha(I_{aa} - I_\alpha)} \cdot \sum_n \frac{\langle 0|\, l_c \,|n\rangle\langle n|\, l_a + P_\alpha^{(n)} \,|0\rangle}{E_0 - E_n}$$

$$G_{\alpha\alpha} = \frac{h}{8\pi^2\, I_\alpha(1 - I_\alpha/I_{aa})} + \frac{h}{4\pi^2\, I_\alpha^2} \cdot \sum_n \frac{|\langle 0|\, P_\alpha^{(n)} \,|n\rangle|^2}{E_0 - E_n} + \frac{h}{4\pi^2\, I_\alpha(I_{aa} - I_\alpha)} \cdot \sum_n \frac{2\,|\langle 0|\, P_\alpha^{(n)} \,|n\rangle|^2 + \langle 0|\, l_a \,|n\rangle\langle n|\, P_\alpha^{(n)} \,|0\rangle + \text{c.c.}}{E_0 - E_n} + \frac{h}{4\pi^2(I_{aa} - I_\alpha)^2} \sum_n \frac{|\langle 0|\, \ell_a + P_\alpha^{(n)} \,|n\rangle|^2}{E_0 - E_n}$$

Throughout this table the electronic matrixelements should read $\langle 0\,|\,\ell_a + \mathscr{P}_\alpha^{(n)}\,|\,n\rangle\langle n\,|\,\ell_b\,|\,0\rangle$ etc. rather than $\langle 0\,|\,l_a + P_\alpha^{(n)}\,|\,n\rangle\langle n\,|\,l_b\,|\,0\rangle$ etc.

Table 2. Theoretical expressions for the elements of the molecular g-matrix (see Eqs. (11c) and (11c')).

$g_{aa} = \frac{M_p}{I_{aa} - I_\alpha} \cdot \left\{ \sum_\nu^{\text{nuclei}} Z_\nu (b_\nu^2 + c_\nu^2) - 3 Z_t r_t^2 \right\} + \frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$	$g_{ab} = \frac{M_p}{I_{bb}} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid l_b \mid 0 \rangle}{E_0 - E_n}$	$g_{ac} = \frac{M_p}{I_{cc}} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid l_c \mid 0 \rangle}{E_0 - E_n}$	$g_{a\alpha} = -\frac{M_p}{I_{aa} - I_\alpha} \left\{ \sum_\nu^{\text{nuclei}} Z_\nu (b_\nu^2 + c_\nu^2) - 3 Z_t r_t^2 \right\} + \frac{M_p}{I_\alpha} 3 Z_t r_t^2 - \frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n} - \frac{M_p}{I_\alpha} \frac{2}{m} \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$
$g_{ba} = + \frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_b \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$	$g_{bb} = \frac{M_p}{I_{bb}} \sum_\nu^{\text{nuclei}} Z_\nu (c_\nu^2 + a_\nu^2) + \frac{M_p}{I_{bb}} \frac{2}{m} \sum_n \frac{\lvert \langle 0 \mid l_b \mid n \rangle \rvert^2}{E_0 - E_n}$	$g_{bc} = \frac{M_p}{I_{cc}} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_b \mid n \rangle \langle n \mid l_c \mid 0 \rangle}{E_0 - E_n}$	$g_{b\alpha} = -\frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_b \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n} - \frac{M_p}{I_\alpha} \frac{2}{m} \sum_n \frac{\langle 0 \mid l_b \mid n \rangle \langle n \mid P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$
$g_{ca} = \frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_c \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$	$g_{cb} = + \frac{M_p}{I_{bb}} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_c \mid n \rangle \langle n \mid l_b \mid 0 \rangle}{E_0 - E_n}$	$g_{cc} = \frac{M_p}{I_{cc}} \sum_\nu^{\text{nuclei}} Z_\nu (a_\nu^2 + b_\nu^2) + \frac{M_p}{I_{cc}} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_c \mid n \rangle \langle n \mid l_c \mid 0 \rangle}{E_0 - E_n}$	$g_{c\alpha} = -\frac{M_p}{I_{aa} - I_\alpha} \frac{2}{m} \cdot \sum_n \frac{\langle 0 \mid l_c \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n} - \frac{M_p}{I_\alpha} \frac{2}{m} \sum_n \frac{\langle 0 \mid l_a \mid n \rangle \langle n \mid P_\alpha^{(n)} \mid 0 \rangle}{E_0 - E_n}$

In this table the electronic matrix elements should read $\langle 0 \mid \ell_a \mid n \rangle \langle n \mid \ell_a + \mathscr{P}_\alpha^{(n)} \mid 0 \rangle$ etc. rather than $\langle 0 \mid l_a \mid n \rangle \langle n \mid l_a + P_\alpha^{(n)} \mid 0 \rangle$ etc. and M_p should be replaced by m_p (proton mass) throughout.

We will begin the treatment of Eq. (18) by considering the first order elements of the perturbation i.e. $\langle j|\langle 0|\mathscr{S}_p|0\rangle|j'\rangle$. Second we will look at those second order contributions which are linear in the magnetic field H_z and thus contribute to the g-matrix. Third we will have to rearrange the obtained expressions so as to cast the result into a form equivalent to the phaenomenological Hamiltonian Equation (11). After completion of this perturbation treatment for $\mathscr{H}_p$, the extension to the complete Hamiltonian is straightforward and may be left to the reader.

A complete listing of the resulting G-, g- and X-matrix elements is given in Tables 1, 2 and 3.

First Order Contributions

Since the operator $P_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial\alpha}$ acts on $|j\rangle = \psi_{JKM}(\Theta, \Phi, \chi)\, e^{im\alpha}/\sqrt{2\pi}$ as well as on $|n\rangle = \varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)$, it is convenient to break it up into two parts:

$$\mathscr{P}_\alpha = \mathscr{P}_\alpha^{(J)} + \mathscr{P}_\alpha^{(n)} \tag{19}$$

where $\mathscr{P}_\alpha^{(J)}$ is supposed to operate on the rotorsional functions only and where $\mathscr{P}_\alpha^{(n)}$ is supposed to operate on the "electronic" wavefunctions only.

We further note two relations:

$$\langle 0|\,\ell_a\,|0\rangle = 0\,, \tag{20}$$

$$\langle 0|\,\mathscr{P}_\alpha^{(n)}\,|0\rangle = 0 \tag{21}$$

where $|0\rangle$ denotes the electronic ground state and where the integration goes over the electron coordinates only.

The first relation follows from the fact that the electronic ground state is nondegenerate and that ℓ_a is a pure imaginary hermitian operator with respect to the electronic wavefunctions. The second follows from the fact that the electronic wavefunctions are normalized to one for every value of the torsional angle:

$$\langle 0|0\rangle = \int \mathrm{d}\tau_{\mathrm{el}}\,|\varphi(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)|^2 \equiv 1\,;$$

$$\mathrm{d}\tau_{\mathrm{el}} = \prod_{\varepsilon}^{\text{electrons}} \mathrm{d}a_\varepsilon\, \mathrm{d}b_\varepsilon\, \mathrm{d}c_\varepsilon\,.$$

Thus

$$\frac{\partial}{\partial\alpha}\langle 0|0\rangle = 0$$

which after an interchange in the sequence of integration over the electron coordinates and differentiation with respect to α leads to

Table 3. Theoretical expressions for the elements of the molecular susceptibility tensor (compare Equation (11d)).

$$\chi_{aa} = -\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon}^{\text{electrons}} b_\varepsilon^2 + c_\varepsilon^2\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}^{\text{ex. states}}\frac{\langle 0|\,l_a\,|n\rangle\langle n|\,l_a\,|0\rangle}{E_0 - E_n}$$

$$\chi_{ab} = +\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon}^{\text{electrons}} a_\varepsilon b_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}^{\text{ex. states}}\frac{\langle 0|\,l_a\,|n\rangle\langle n|\,l_b\,|0\rangle}{E_0 - E_n}$$

$$\chi_{ac} = +\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon}^{\text{electrons}} a_\varepsilon c_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}^{\text{ex. states}}\frac{\langle 0|\,l_a\,|n\rangle\langle n|\,l_c\,|0\rangle}{E_0 - E_n}$$

$$\chi_{ba} = +\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon} b_\varepsilon a_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_b\,|n\rangle\langle n|\,l_a\,|0\rangle}{E_0 - E_n}$$

$$\chi_{bb} = -\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon}(c_\varepsilon^2 + a_\varepsilon^2)\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_b\,|n\rangle\langle n|\,l_b\,|0\rangle}{E_0 - E_n}$$

$$\chi_{bc} = +\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon} b_\varepsilon c_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_b\,|n\rangle\langle n|\,l_c\,|0\rangle}{E_0 - E_n}$$

$$\chi_{ca} = +\frac{e^2}{4mc^2}\langle 0|\sum c_\varepsilon a_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_c\,|n\rangle\langle n|\,l_a\,|0\rangle}{E_0 - E_n}$$

$$\chi_{cb} = +\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon} a_\varepsilon b_\varepsilon\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_c\,|n\rangle\langle n|\,l_b\,|0\rangle}{E_0 - E_n}$$

$$\chi_{cc} = -\frac{e^2}{4mc^2}\langle 0|\sum_{\varepsilon} a_\varepsilon^2 + b_\varepsilon^2\,|0\rangle - \frac{e^2}{2m^2c^2}\sum_{n}\frac{\langle 0|\,l_c\,|n\rangle\langle n|\,l_c\,|0\rangle}{E_0 - E_n}$$

The electronic matrixelements should read $\langle 0|\,\ell_a\,|n\rangle$ etc. rather than $\langle 0|\,l_a\,|n\rangle$ etc.

$$\frac{\partial}{\partial\alpha}\langle 0|0\rangle = 2\langle 0|\frac{\partial}{\partial\alpha}|0\rangle = 0$$

or

$$\langle 0|\mathscr{P}_\alpha^{(n)}|0\rangle = 0\,. \quad \text{q.e.d.}$$

Again the fact that φ_n is nondegenerate was used (otherwise the only conclusion that could be drawn would be that the real part of $\langle 0|\frac{\partial}{\partial\alpha}|0\rangle$ were zero). From Eqs. (18), (20) and (21), if inserted into (17), the first order contributions follow as:

$$\langle j|\langle 0|\mathscr{S}_p|0\rangle|j'\rangle = E_0\,\delta_{jj'} + \langle j|\varepsilon_0(\alpha)|j'\rangle \quad (22a)$$

$$+\frac{\langle j|\mathscr{P}_a{}^2|j'\rangle}{2(I_{aa}-I_\alpha)} - \frac{\langle j|\mathscr{P}_a\mathscr{P}_\alpha^{(j)}+\mathscr{P}_\alpha^{(j)}\mathscr{P}_a|j'\rangle}{2(I_{aa}-I_\alpha)}$$

$$+\frac{\langle j|\mathscr{P}_\alpha^{(j)2}|j'\rangle}{2I_\alpha(1-I\alpha/I_{aa})} \quad (22b)$$

$$+\frac{\langle j|\langle 0|\mathscr{P}_\alpha^{(n)2}|0\rangle|j'\rangle}{2I_\alpha(1-I_\alpha/I_{aa})} + \frac{\langle j|\langle 0|\ell_a{}^2|0\rangle|j'\rangle}{2(I_{aa}-I_\alpha)}$$

$$+\frac{\langle j|\langle 0|\mathscr{P}_\alpha^{(n)}\ell_a+\ell_a\mathscr{P}_\alpha^{(n)}|0\rangle|j'\rangle}{2(I_{aa}-I_\alpha)}\,. \quad (22c)$$

From Eq. (22b) one obtains contributions to the G_{aa}, $G_{a\alpha}$, $G_{\alpha a}$ and $G_{\alpha\alpha}$ elements of the rotational constants matrix. Eq. (22c) leads to a contribution to the effective potential for the internal rotation. If we assume that the electronic ground state expectation values for the squares of the angular momentum operators may be on the order of $10\hbar^2$ the absolute value of the contributions due to (22c) might be on the order of 100 cal/mole. Its α-dependent part however will be considerably smaller, so that we believe that the effective barrier is still essentially given by $\varepsilon_n(\alpha)$, the α-dependent part of the electronic eigenvalue.

Second Order Contributions

From the second order perturbation sums, Eq. (17), one gets contributions which are linear in the magnetic field and others which are quadratic. The first correspond to contributions due to the g-matrix of the effective rotorsional Hamiltonian, the latter to contributions due to the molecular susceptibility tensor. For the simplified Hamiltonian $\mathscr{H}_p$ (see Eq. (18)) there is only one second order contribution which is quadratic in H_z. It is given by Equation (23).

$$\frac{e^2}{4m^2c^2}H_z^2\sum_{n''}^{\text{excited states}}\sum_{j''}\frac{\langle j|\langle 0|[l_a\cos aZ]|n''\rangle|j''\rangle\langle j''|\langle n''|[l_a\cos aZ]|0\rangle|j'\rangle}{E_0-E_{n''}} \quad (23a)$$

$$=\frac{e^2}{4m^2c^2}H_z^2\langle j|[\cos^2 aZ]\sum_{n''}\frac{\langle 0|\ell_a|n''\rangle\langle n''\ell_a|0\rangle}{E_0-E_n}|j'\rangle \quad (23b)$$

$$=-\tfrac{1}{2}H_z^2\langle j|[\cos^2 aZ]\,\chi_{aa}^{(p)}|j'\rangle \quad (23c)$$

with

$$\chi_{aa}^{p} = -\frac{e^2}{2m^2c^2}\sum_{n''}^{\text{excited states}}\frac{\langle 0|\ell_a|n''\rangle\langle n''|\ell_a|0\rangle}{E_0-E_{n''}} \quad \text{(compare Table 2).} \quad (24)$$

In the step from (23a) to (23b) use is made of the relation:

$$\sum_{j''}\langle j|\langle 0|[l_a\cos aZ]|n''\rangle|j''\rangle\langle j''|\langle n''|[l_a\cos aZ]|0\rangle|j'\rangle$$
$$=\langle j|\langle 0|[l_a\cos aZ]|n''\rangle\langle n''|[l_a\cos aZ]|0\rangle|j'\rangle$$

(completeness of the $e^{im\alpha}$-Basis with respect to all functions periodic in α), and of the fact that $[\cos aZ]$ does not operate on the electronic wavefunctions and may thus be pulled out of the matrix elements $\langle 0|[l_a\cos aZ]|n''\rangle$ and $\langle n''|[l_a\cos aZ]|0\rangle$. We note that the expression for the paramagnetic susceptibility χ_{aa}^p defined by Eq. (24) is the same as in the rigid rotor case. The only difference is that χ_{aa}^p is no more to be regarded as a constant molecular parameter, but as a function of the torsional angle α.

We now turn to the second order contributions which are linear in the magnetic field strength. From their general definition Eq. (17) and the Hamiltonian under consideration, Eq. (18), they follow as given in Eq. (25):

$$H_z \frac{e}{2mc}\Bigg(-\frac{1}{(I_{aa}-I_\alpha)}\Bigg[\sum_{n'',j''}\frac{\langle j|\mathscr{P}_a\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.1}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle\mathscr{P}_a|j'\rangle}{E_0-E_{n''}}\Bigg]$$

$$-\frac{1}{(I_{aa}-I_\alpha)}\Bigg[\sum_{n'',j''}\frac{\langle j|\mathscr{P}_a\langle 0|\mathscr{P}_\alpha^{(n)}|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.1'}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\mathscr{P}_\alpha^{(n)}|0\rangle\mathscr{P}_a|j'\rangle}{E_0-E_{n''}}\Bigg]$$

$$+\frac{1}{(I_{aa}-I_\alpha)}\Bigg[\sum_{n'',j''}\frac{\langle j|\langle 0|\ell_a|n''\rangle\mathscr{P}_\alpha^{(j)}|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.2}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle\mathscr{P}_\alpha^{(j)}|j'\rangle}{E_0-E_{n''}}\Bigg]$$

$$+\frac{1}{(I_{aa}-I_\alpha)}\Bigg[\sum_{n'',j''}\frac{\langle j|\langle 0|\ell_a\mathscr{P}_\alpha^{(n)}|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.3}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a\mathscr{P}_\alpha^{(n)}|0\rangle|j'\rangle}{E_0-E_{n''}}\Bigg]$$

$$+\frac{1}{I_\alpha(1-I_\alpha/I_{aa})}\Bigg[\sum_{n'',j''}\frac{\langle j|\langle 0|\mathscr{P}_\alpha^{(n)}|n''\rangle\mathscr{P}_\alpha^{(j)}|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.4}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\mathscr{P}_\alpha^{(n)}|0\rangle\mathscr{P}_\alpha^{(j)}|j'\rangle}{E_0-E_{n''}}\Bigg]$$

$$+\frac{1}{2I_\alpha(1-I_\alpha/I_{aa})}\Bigg[\sum_{n'',j''}\frac{\langle j|\langle 0|\mathscr{P}_\alpha^{(n)2}|n''\rangle|j''\rangle\langle j''|\langle n''|\ell_a|0\rangle[\cos a Z]|j'\rangle}{E_0-E_{n''}} \tag{25.5}$$

$$+\sum_{n'',j''}\frac{\langle j|[\cos a Z]\langle 0|\ell_a|n''\rangle|j''\rangle\langle j''|\langle n''|\mathscr{P}_\alpha^{(n)2}|0\rangle|j'\rangle}{E_0-E_{n''}}\Bigg]\Bigg).$$

With $\langle 0|\mathscr{P}_\alpha^{(n)}|n''\rangle = \langle n''|\mathscr{P}_\alpha^{(n)}|0\rangle^*$ [see App. Eq. (A.1)] and $\langle 0|\ell_a|n''\rangle = \langle n''|\ell_a|0\rangle^*$ parts (25.1) and (25.1′) already have the structure required for immediate transscription into a contribution to the effective rotorsional Hamiltonian which imitates the complete Hamiltonian as far as the electronic ground state is concerned. They are equivalent to the j, j'-matrixelements of

$$-\frac{\mu_N H_z}{2}\left([\cos a Z]\, g_{aa}^{el}\, \mathscr{J}_a + \mathscr{J}_a\, g_{aa}^{el*}\,[\cos a Z]\right)$$

with

$$g_{aa}^{(el)} = \frac{m_p}{I_{aa}-I_\alpha}\frac{2}{m} \qquad \text{(compare Table 2)}$$

$$\cdot\sum_{n''}^{\substack{\text{excited}\\ \text{states}}}\frac{\langle 0|\ell_a|n''\rangle\langle n''|\ell_a+\mathscr{P}_\alpha^{(n)}|0\rangle}{E_0-E_{n''}},$$

(again, via the α-dependence of the electronic wavefunctions g_{aa}^{el} does depend on the torsional angle α, at least in principle).

In parts (25.2) through (25.5) it is not so evident that they may be rearranged so as to lead to Hermitian contributions to an effective rotorsional Hamiltonian such as given by Equation (11). The reason is that they include the operator $\mathscr{P}_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial\alpha}$ which cannot be simply shifted to the front or rear of the sums running over the excited electronic states without introducing the appropriate corrections. In (25.2) it is the first sum which needs special consideration. If we shift $\mathscr{P}_a$ in front of the α-dependent electronic matrixelement $\langle 0|\ell_a|n''\rangle$ (where it should be positioned in the effective

Hamiltonian), we have to correct for the introduced error by subtracting

$$H_z \frac{e}{2mc} \cdot \frac{1}{(I_{aa} - I_\alpha)} \sum_{n'',j''} \frac{\langle j | [\mathscr{P}_\alpha \langle 0 | \ell_a | n'' \rangle] | j'' \rangle \langle j'' | \langle n'' | \ell_a | 0 \rangle [\cos a Z] | j' \rangle}{E_0 - E_{n''}}$$

where the square bracket indicates that $\mathscr{P}_\alpha$ operates only on $\langle 0 | \ell_a | n'' \rangle$. Fortunately, via Eq. (A.2) of the Appendix this correction combines favourably with the first sum of part (25.3):

$$\begin{aligned} & H_z \frac{e}{2mc} \frac{1}{(I_{aa} - I_\alpha)} \Bigg[\overbrace{\sum_{n'',j''} \frac{\langle j | \langle 0 | \ell_a \mathscr{P}_\alpha^{(n)} | n'' \rangle | j'' \rangle \langle j'' | \langle n'' | \ell_a | 0 \rangle | j' \rangle}{E_0 - E_{n''}}}^{\text{from (25,3)}} \\ & \quad - \overbrace{\sum_{n'',j''} \frac{\langle j | [\mathscr{P}_\alpha \langle 0 | \ell_a | n'' \rangle] | j'' \rangle \langle j'' | \langle n'' | \ell_a | 0 \rangle [\cos a Z] | j' \rangle}{E_0 - E_{n''}}}^{\text{from the correction}} \Bigg] \\ & = H_z \frac{e}{2mc} \frac{1}{(I_{aa} - I_\alpha)} \sum_{n'',j''} \frac{\langle j | \langle n'' | \ell_a \mathscr{P}_\alpha^{(n)} | 0 \rangle^* | j'' \rangle \langle j'' | \langle n'' | \ell_a | 0 \rangle [\cos a Z] | j' \rangle}{E_0 - E_{n''}} . \end{aligned} \tag{26}$$

Thus after summation over j'' (25.2) and (25.3) combine to the following contribution to the effective rotorsional Hamiltonian:

$$- \mu_N H_z ([\cos a Z] \tilde{g}_{a\alpha} \mathscr{J}_\alpha + \mathscr{J}_\alpha \tilde{g}_{a\alpha}^* [\cos a Z]) + \mu_N H_z ([\cos a Z] c_{a\alpha} + c_{a\alpha}^* [\cos a Z]) , \tag{27}$$

with

$$\tilde{g}_{a\alpha} = - \frac{m_p}{I_{aa} - I_\alpha} \cdot \frac{2}{m} \sum_{n''} \frac{\langle 0 | \ell_a | n'' \rangle \langle n'' | \ell_a | 0 \rangle}{E_0 - E_{n''}} \tag{27.1}$$

and

$$c_{a\alpha} = \frac{m_p}{I_{aa} - I_\alpha} \cdot \frac{2}{m} \sum_{n''} \frac{\langle 0 | \ell_a | n'' \rangle \langle n'' | \ell_a \mathscr{P}_\alpha^{(n)} | 0 \rangle}{E_0 - E_{n''}} . \tag{27.2}$$

While Eq. (27.1) leads to a contribution to the $a\alpha$-element of the molecular g-matrix (see Table 2), the contribution arising from Eq. (27.2) vanishes for molecules with nondegenerate electronic states for which it is purely imaginary and is compensated by its complex conjugate in Equation (27).

Finally we turn to parts (25.4) and (25.5). In (25.4) it is again the first sum in which the torsional operator $\mathscr{P}_\alpha$ can not be shifted in front of the α-dependent matrix element $\langle 0 | \mathscr{P}_\alpha^{(n)} | n'' \rangle$ without a correction:

$$\langle 0 | \mathscr{P}_\alpha^{(n)} | n'' \rangle \mathscr{P}_\alpha^{(j)} \triangleq \mathscr{P}_\alpha \langle 0 | \mathscr{P}_\alpha^{(n)} | n'' \rangle - [\mathscr{P}_\alpha \langle 0 | \mathscr{P}_\alpha^{(n)} | n'' \rangle] .$$

In this case the correction combines via Eq. (A.3) with the leading sum in (25.5) such that (25.4) and (25.5) together may be arranged to give:

$$\begin{aligned} & H_z \frac{e}{2mc} \frac{1}{I_\alpha (1 - I_\alpha / I_{aa})} \Bigg[\langle j | [\cos a Z] \sum_{n''} \frac{\langle 0 | \ell_a | n'' \rangle \langle n'' | \mathscr{P}_\alpha^{(n)} | 0 \rangle}{E_0 - E_{n''}} \mathscr{P}_\alpha | j' \rangle \\ & \qquad + \langle j | \mathscr{P}_\alpha \sum_{n''} \frac{\langle 0 | \mathscr{P}_\alpha^{(n)} | n'' \rangle \langle n'' | \ell_a | 0 \rangle}{E_0 - E_{n''}} [\cos a Z] | j' \rangle \Bigg] \end{aligned} \tag{28.1}$$

$$\begin{aligned} & + H_z \frac{e}{2mc} \frac{1}{I_\alpha (1 - I_\alpha / I_{aa})} \Bigg[\langle j | [\cos a Z] \sum_{n''} \frac{\langle 0 | \ell_a | n'' \rangle \langle n'' | \mathscr{P}_\alpha^{(n)2} | 0 \rangle}{E_0 - E_{n''}} | j' \rangle \\ & \qquad + \langle j | \sum_{n''} \frac{\langle n'' | \mathscr{P}_\alpha^{(n)2} | 0 \rangle^* \langle n'' | \ell_a | 0 \rangle}{E_0 - E_{n''}} [\cos a Z] | j' \rangle \Bigg] . \end{aligned} \tag{28.2}$$

For molecules with nondegenerate electronic states the square bracket in (28.2) must vanish because in this case the two sums are purely imaginary and compensate each other, while (28.1) is equivalent to the j, j'-matrixelement of the following part of the effective rotorsional Hamiltonian:

$$-\mu_N[[\cos a\, Z]\,\tilde{\tilde{g}}^{el}_{a\alpha}\,\mathcal{J}_\alpha + \mathcal{J}_\alpha\,\tilde{\tilde{g}}^{el*}_{a\alpha}\,[\cos a\, Z]] \quad (29)$$

with

$$\begin{aligned}\tilde{\tilde{g}}^{el}_{a\alpha} &= -\frac{m_p}{I_\alpha(1-I_\alpha/I_{aa})}\frac{2}{m}\\ &\quad\cdot\sum_{n''}\frac{\langle 0|\,\ell_a\,|n''\rangle\langle n''|\,\mathcal{P}_\alpha^{(n)}\,|0\rangle}{E_0-E_{n''}} \qquad (30)\\ &= -\frac{m_p}{I_{aa}-I_\alpha}\frac{2}{m}\sum_{n''}\frac{\langle 0|\,\ell_a\,|n''\rangle\langle n''|\,\mathcal{P}_\alpha^{(n)}\,|0\rangle}{E_0-E_{n''}}\\ &\quad-\frac{m_p}{I_\alpha}\frac{2}{m}\sum_{n''}\frac{\langle 0|\,\ell_a\,|n''\rangle\langle n''|\,\mathcal{P}_\alpha^{(n)}\,|0\rangle}{E_0-E_{n''}}\end{aligned}$$

(see Table 2).

If one looks at the complete set of theoretical expressions thus obtained for the molecular g-values (Table 2), and molecular susceptibilities (Table 3), and if one compares the results with those obtained for rigid rotor molecules, it is evident that for molecules with internal rotation the theoretical expressions for the molecular electric quadrupole moments, for the paramagnetic susceptibilities, for the anisotropies of the second moments of the electron charge distribution, and for the electric dipole moment [24] may be obtained from the corresponding rigid rotor formulae if only $g_{aa}I_{aa}$ in the latter is replaced by $g_{aa}I_{aa}+g_{a\alpha}I_\alpha$. (For convenience of the reader the rigid rotor expressions are listed in Table 4.) We recall that C_{2v} symmetry of the frame was assumed in our derivation, with the internal rotation axis coinciding with the molecular a-axis. We also note that in the analysis of the Zeeman data it will be a resonable approximation to neglect the electronic contributions to the

Table 4. Rigid rotor expressions for the rotational constants and for the diagonal elements of the molecular g- and χ-tensors are listed in the upper three rows. At the bottom of the table expressions are listed for molecular parameters which may be derived from the experimentally determined Zeeman parameters. For a molecule like $CH_3{-}NO_2$ with a low barrier internal rotation about the a-principal inertia axis and with C_{2v} symmetry of the frame, the corresponding expressions for the derived quantities may be obtained if $g_{aa}I_{aa}$ in the rigid rotor expressions is replaced by $g_{aa}I_{aa}+g_{a\alpha}I_\alpha$ (see Tables 2 and 3). $(\gamma, \gamma', \gamma'') = (a, b, c)$ and cyclic permutations.

$$G_{\gamma\gamma} = \frac{h}{8\pi^2 I_{\gamma\gamma}} \quad \text{with} \quad I_{\gamma\gamma} = \sum_\nu^{\text{nuclei}} m_\nu(\gamma_\nu'^2+\gamma_\nu''^2)$$

$$g_{\gamma\gamma} = \frac{m_p}{I_{\gamma\gamma}}\left\{\sum_\nu^{\text{nuclei}} Z_\nu(\gamma_\nu'^2+\gamma_\nu''^2) + \frac{2}{m}\sum_n^{\text{ex. states}}\frac{\langle 0|\,l_\gamma\,|n\rangle\langle n|\,l_\gamma\,|0\rangle}{E_0-E_n}\right\}$$

$$\chi_{\gamma\gamma} = -\frac{e^2}{4mc^2}\left\{\langle 0|\sum_\varepsilon^{\text{electrons}}(\gamma_\varepsilon'^2+\gamma_\varepsilon''^2)\,|0\rangle + \frac{2}{m}\sum_n^{\text{ex. states}}\frac{\langle 0|\,l_\gamma\,|n\rangle\langle n|\,l_\gamma\,|0\rangle}{E_0-E_n}\right\}$$

molecular electric quadrupole moments:

$$\begin{aligned}Q_{\gamma\gamma} &= \frac{e}{2}\left\{\sum_\nu^{\text{nuclei}} Z_\nu(2\gamma_\nu^2-\gamma_\nu'^2-\gamma_\nu''^2) - \langle 0|\sum_\varepsilon^{\text{electrons}}(2\gamma_\varepsilon^2-\gamma_\varepsilon'^2-\gamma_\varepsilon''^2)\,|0\rangle\right\}\\ &= -\frac{e}{2m_p}\{2g_{\gamma\gamma}I_{\gamma\gamma}-g_{\gamma'\gamma'}I_{\gamma'\gamma'}-g_{\gamma''\gamma''}I_{\gamma''\gamma''}\} - \frac{2mc^2}{e^2}\{2\chi_{\gamma\gamma}-\chi_{\gamma'\gamma'}-\chi_{\gamma''\gamma''}\}\end{aligned}$$

paramagnetic susceptibilities:

$$\chi^p_{\gamma\gamma} = -\frac{e^2}{2m^2c^2}\sum_n^{\text{ex. states}}\frac{\langle 0|\,l_\gamma\,|n\rangle\langle n|\,l_\gamma\,|0\rangle}{E_0-E_n} = -\frac{e^2}{4mc^2}\left\{\frac{g_{\gamma\gamma}I_{\gamma\gamma}}{m_p} - \sum_\nu^{\text{nuclei}} Z_\nu(\gamma_\nu'^2+\gamma_\nu''^2)\right\}$$

anisotropies of the second moments of the electron charge distribution:

$$\langle 0|\sum_\varepsilon^{\text{electrons}}(\gamma_\varepsilon^2-\gamma_\varepsilon'^2)\,|0\rangle = \sum_\nu^{\text{nuclei}} Z_\nu(\gamma_\nu^2-\gamma_\nu'^2) + (g_{\gamma\gamma}I_{\gamma\gamma}-g_{\gamma'\gamma'}I_{\gamma'\gamma'})/m_p + \frac{4mc^2}{e^2}(\chi_{\gamma\gamma}-\chi_{\gamma'\gamma'})$$

molecular electric dipole moment:

$$\mu_a = \frac{1}{\Delta a}\frac{e}{2m_p}(g'_{bb}I'_{bb}-g_{bb}I_{bb}) = \frac{1}{\Delta a}\cdot\frac{e}{2m_p}(g'_{cc}I'_{cc}-g_{cc}I_{cc})$$

(assumption: the center of mass has been shifted along the a-axis due to isotopic substitution such that the coordinates have changed to $a_\nu' = a_\nu + \Delta a$ and $a_\varepsilon' = a_\varepsilon + \Delta a$ respectively. $g'_{\gamma\gamma}$ and $I'_{\gamma\gamma}$ are the g-values and moments of inertia of the isotopically substituted molecule).

rotational constants i.e. to set $(I_{aa} - I_\alpha) = \dfrac{h}{8\pi^2 G_{aa}}$ etc., and to use as moments of inertia those obtained in the standard way from the analysis of the torsional fine structure in the zero field rotational spectrum. If one wants to go beyond this approximation, one should include the zero point vibrations in the treatment. Their neglection is probably more serious than the neglection of the electronic perturbation sums in the theoretical expressions for the rotational constants. Problems encountered in the determination of the sign of the electric dipole moment in rigid rotor molecules strongly point into this direction [25].

IV. The α-Dependence of the Molecular Parameters in the Effective Rotorsional Hamiltonian

For the analysis of observed Zeeman spectra of low barrier molecules it is essential to know some general features of the α-dependence of the molecular parameters. To investigate those, we have to resort to the theoretical expressions given in Tables 1, 2, and 3. Since all theoretical expressions involve electronic expectation values and (or) perturbation sums, we will first study some symmetries which relate the electronic Schrödinger equations, eigenfunctions and eigenvalues for certain distinct α-positions. In the course of this discussion we will use the language of group theory, but we note that the "symmetry operations" used will not be symmetry operations of an electronic Hamiltonian in the usual sense, but will relate the electronic Hamiltonians for different nuclear configurations. As in the previous sections we assume the rigid top rigid frame model to be valid. We further assume C_{3v}-symmetry for the top and C_{2v}-symmetry for the frame. Then the α-dependence of the molecular parameters derives from the following two facts.

1. Due to the C_{3v}-symmetry of the top, the nuclear configuration is reproduced by every $2\pi/3$ revolution of the top about its symmetry axis. Thus, in principle, all molecular parameters may be expanded into Fourier series with period $2\pi/3$:

$$f(\alpha) = a_0 + \sum_{n=1}^{\infty} a_n \cos(3n\alpha) + \sum_{n=1}^{\infty} b_n \sin(3n\alpha) \tag{31}$$

($f(\alpha)$ = shorthand for the molecular parameter under consideration).

2. The C_{2v}-symmetry of the frame puts further restraints on the Fourier expansions, so that — depending on the individual molecular parameter under consideration — some of the expansion coefficients in Eq. (31) necessarily vanish. In what follows we will study this point in more detail.

To start with we note that the change of the torsional angle from a value α to the three values $\alpha+\pi$ or $-\alpha$ or $-\alpha+\pi$ leads to nuclear configurations, which in a certain sense are equivalent to the original configuration (see Figure 3). To be more specific, the three new configurations might also have been generated from the original one by a C_{2a}-rotation of the nuclear frame about the a-axis, by a (non feasible) reflection at the ab-plane, and by a (equally nonfeasible) reflection at the ac-plane respectively. (It is only charge and position of the nuclei that counts in the electronic Schrödinger equation.) As a result the electronic Schrödinger equations for the nuclear configurations described by the above α-values may be transformed into each other by application of the corresponding transformations now acting only on the electronic coordinates i.e.:

$$\mathscr{C}_{2a}^{\mathrm{el}}\,\mathscr{H}_{\mathrm{el},\alpha} = \mathscr{H}_{\mathrm{el},\alpha+\pi} \quad \text{with} \quad \begin{aligned} \mathscr{C}_{2a}^{\mathrm{el}}\, a_\varepsilon &\Rightarrow a_\varepsilon\,, \\ \mathscr{C}_{2a}^{\mathrm{el}}\, b_\varepsilon &\Rightarrow -b_\varepsilon\,, \\ \mathscr{C}_{2a}^{\mathrm{el}}\, c_\varepsilon &\Rightarrow -c_\varepsilon\,, \end{aligned} \tag{32}$$

$$m_{ab}^{\mathrm{el}}\,\mathscr{H}_{\mathrm{el},\alpha} = \mathscr{H}_{\mathrm{el},-\alpha} \quad \text{with} \quad \begin{aligned} m_{ab}^{\mathrm{el}}\, a_\varepsilon &\Rightarrow a_\varepsilon\,, \\ m_{ab}^{\mathrm{el}}\, b_\varepsilon &\Rightarrow b_\varepsilon\,, \\ m_{ab}^{\mathrm{el}}\, c_\varepsilon &\Rightarrow -c_\varepsilon\,, \end{aligned} \tag{33}$$

$$m_{ac}^{\mathrm{el}}\,\mathscr{H}_{\mathrm{el},\alpha} = \mathscr{H}_{\mathrm{el},-\alpha+\pi} \quad \text{with} \quad \begin{aligned} m_{ac}^{\mathrm{el}}\, a_\varepsilon &\Rightarrow a_\varepsilon\,, \\ m_{ac}^{\mathrm{el}}\, b_\varepsilon &\Rightarrow -b_\varepsilon\,, \\ m_{ac}^{\mathrm{el}}\, c_\varepsilon &\Rightarrow c_\varepsilon\,. \end{aligned} \tag{34}$$

As an example, application of the operation $\mathscr{C}_{2a}^{\mathrm{el}}$ to the electronic Schrödinger equation corresponding to the nuclear configuration with torsional angle α leads to the electronic Schrödinger equation corresponding to the torsional angle $\alpha+\pi$.

$$\mathscr{C}_{2a}^{\mathrm{el}} \quad \begin{aligned} &\mathscr{H}_{\mathrm{el},\alpha}\,\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots) \\ &\quad = E_n(\alpha)\,\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots), \end{aligned} \tag{35}$$

$$\begin{aligned} &\mathscr{H}_{\mathrm{el},\alpha+\pi}\,\varphi_n(\alpha;\ldots;a_\varepsilon,-b_\varepsilon,-c_\varepsilon,\ldots) \\ &\quad = E_n(\alpha)\,\varphi_n(\alpha;\ldots;a_\varepsilon,-b_\varepsilon,-c_\varepsilon,\ldots). \end{aligned} \tag{36}$$

As a result the function $\varphi_n(\alpha;\ldots;a_\varepsilon,-b_\varepsilon,-c_\varepsilon,\ldots)$ is solution of the electronic Schrödinger equation

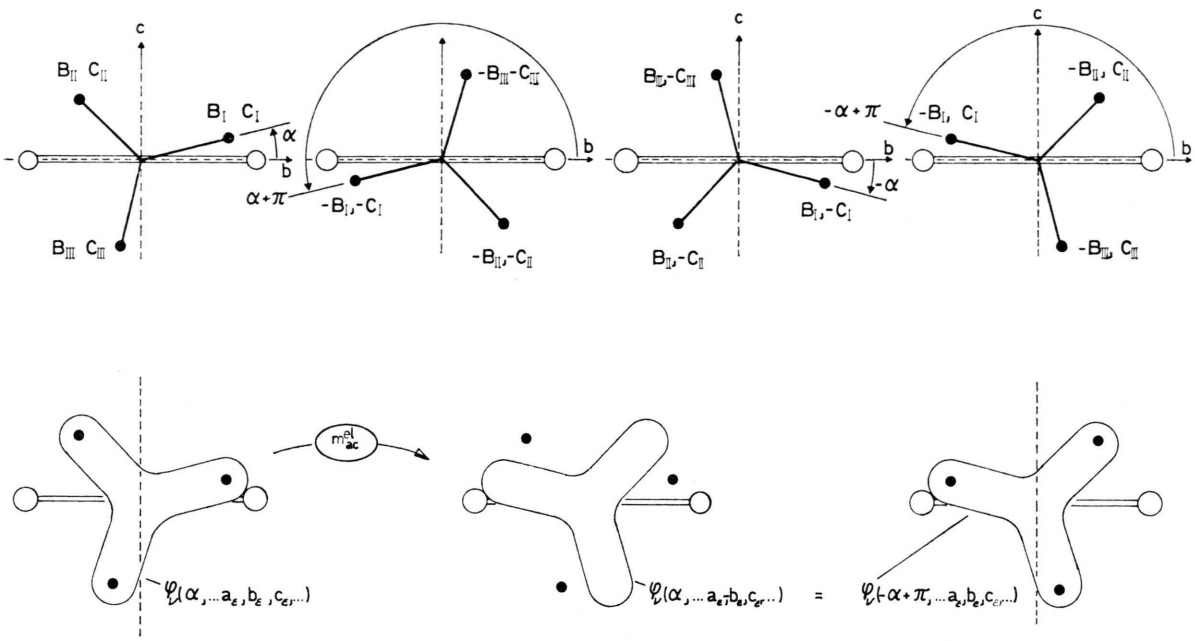

Fig. 3. In molecules such as Nitromethane, here depicted in a view along the C-N-bond, there are for each nonzero torsional angle α three more α-values, which correspond to "essentially equivalent" nuclear configurations (upper row). "Essentially equivalent" in this context means, that their electronic eigenvalues are identical and that their electronic eigenfunctions may be transformed into each other by application of the operations $\mathscr{C}_{2a}^{el}$: $a_\varepsilon \to a_\varepsilon$, $b_\varepsilon \to -b_\varepsilon$, $c_\varepsilon \to -c_\varepsilon$; m_{ab}^{el}: $a_\varepsilon \to a_\varepsilon$, $b_\varepsilon \to b_\varepsilon$, $c_\varepsilon \to -c_\varepsilon$; m_{ac}^{el}: $a_\varepsilon \to a_\varepsilon$, $b_\varepsilon \to -b_\varepsilon$, $c_\varepsilon \to c_\varepsilon$. The latter is shown schematically in the lower row.

for the $\alpha+\pi$ nuclear configuration, and, since apart from the accidental degeneracies the electronic states are nondegenerate due to the low symmetry of the nuclear frame, the operation $\mathscr{C}_{2a}^{el}$ generates a one to one relationship between the electronic eigenvalues and eigenfunctions for torsional angles α and $\alpha+\pi$:

$$E_n(\alpha+\pi) = E_n(\alpha)\,, \tag{37}$$

$$\varphi_n(\alpha+\pi;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots) = p_{n,C_{2a}}\varphi_n(\alpha;\ldots;a_\varepsilon,-b_\varepsilon,-c_\varepsilon,\ldots)\,. \tag{38}$$

In (38) we have, as a safety measure, introduced a phase factor $p_{n,C_{2a}}$ ($|p_{n,C_{2a}}|=1$), to guarantee that the above defined $\varphi_n(\alpha+\pi;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)$ be identical with the one that would be obtained if the torsional angle were continuously changed from α to $\alpha+\pi$. Since the phase factors drop out in the expectation values and perturbation sums (see below) we need not to discuss them further in this context.

In a similar manner the operations m_{ab}^{el} and m_{ac}^{el} generate the following relations:

$$E_n(-\alpha) = E_n(\alpha)\,, \tag{39}$$

$$\varphi_n(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots) = p_{n,m_{ab}}\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,-c_\varepsilon,\ldots),\ |p_{n,m_{ab}}|=1, \tag{40}$$

and

$$E_n(-\alpha+\pi) = E_n(\alpha)\,, \tag{41}$$

$$\varphi_n(-\alpha+\pi;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots) = p_{n,m_{ac}}\varphi_n(\alpha;\ldots;a_\varepsilon,-b_\varepsilon,c_\varepsilon,\ldots),\ |p_{n,m_{ac}}|=1. \tag{42}$$

Since the relations (37) through (42) will bear on the dependence of the molecular parameters on α, it is at this stage useful to introduce a corresponding group of operations acting only on the torsional angle and transforming the α-values for the "equivalent" nuclear configurations into each other:

$$\mathscr{C}_{2a}^{\alpha}\,\alpha \Rightarrow \alpha+\pi,$$
$$m_{ab}^{\alpha}\,\alpha \Rightarrow -\alpha,\quad m_{ac}^{\alpha}\,\alpha \Rightarrow -\alpha+\pi\,. \tag{43}$$

If complemented by the unit operation, this set of transformations is isomorphous to the group C_{2v}. In what follows we will show that relations (37) through (42) may be used to deduce that — under the above group of α-transformations — each molecular parameter transforms according to one

out of the four irreducible representations of group C_{2v}.

To this end we will first use Eqs. (38), (40), and (42) to relate for torsional angles $\alpha+\pi$, $-\alpha$ and $-\alpha+\pi$ the electronic matrix elements of any operator of interest here to the corresponding values for the torsional angle α. Exemplarily we will carry out the calculation for the position $-\alpha$ and for the operators

$$\ell_a = \frac{\hbar}{i}\sum_\varepsilon b_\varepsilon \frac{\partial}{\partial c_\varepsilon} - c_\varepsilon \frac{\partial}{\partial b_\varepsilon} \quad \text{and} \quad \mathscr{P}_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial \alpha}.$$

We will treat ℓ_a first.

Starting point is the definition of the matrix element as integral over the electron coordinates:

$$\langle 0|\,\ell_a\,|n\rangle_{(\alpha)} = \int \varphi_0^*(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\frac{\hbar}{i}\sum_\varepsilon\left(b_\varepsilon\frac{\partial}{\partial c_\varepsilon} - c_\varepsilon\frac{\partial}{\partial b_\varepsilon}\right)\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\,\mathrm{d}\tau_{\mathrm{el}}, \tag{44}$$

$$\langle 0|\,\ell_a\,|n\rangle_{(-\alpha)} = \int \varphi_0^*(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\frac{\hbar}{i}\sum_\varepsilon\left(b_\varepsilon\frac{\partial}{\partial c_\varepsilon} - c_\varepsilon\frac{\partial}{\partial b_\varepsilon}\right)\varphi_n(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\,\mathrm{d}\tau_{\mathrm{el}}. \tag{45}$$

To relate the two matrix elements we use Eq. (40) to express the electronic eigenfunctions for position $-\alpha$ by those for position α:

$$\langle 0|\,\ell_a\,|n\rangle_{(-\alpha)} = p^*_{0,m_{ab}}p_{n,m_{ab}}\int\varphi_0^*(\alpha;\ldots a_\varepsilon,b_\varepsilon,-c_\varepsilon,\ldots)\frac{\hbar}{i}\sum_\varepsilon\left(b_\varepsilon\frac{\partial}{\partial c_\varepsilon} - c_\varepsilon\frac{\partial}{\partial b_\varepsilon}\right) \cdot\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,-c_\varepsilon\ldots)\,\mathrm{d}\tau_{\mathrm{el}}. \tag{46}$$

Upon application of the transformation m^{el}_{ab} (Eq. (33)) this integral transforms to

$$-p^*_{0,m_{ab}}p_{n,m_{ab}}\int\varphi_0^*(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\frac{\hbar}{i}\sum_\varepsilon\left(b_\varepsilon\frac{\partial}{\partial c_\varepsilon} - c_\varepsilon\frac{\partial}{\partial b_\varepsilon}\right)\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\,\mathrm{d}\tau_{\mathrm{el}} \tag{47}$$

or

$$\langle 0|\,\ell_a\,|n\rangle_{(-\alpha)} = -p^*_{0,m_{ab}}p_{n,m_{ab}}\langle 0|\,\ell_a\,|n\rangle_{(\alpha)}. \tag{48}$$

Second we will treat the operator $\mathscr{P}_\alpha$. Again we will compare electronic matrix elements calculated for the torsional angles α and $-\alpha$. From the definition of $\mathscr{P}_\alpha$ we have: (49)

$$\mathscr{P}_\alpha\varphi_n(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots) = \frac{\hbar}{i}\lim_{\Delta\alpha\to 0}\frac{\varphi_n(-\alpha+\Delta\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)-\varphi_n(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)}{\Delta\alpha}.$$

With the use of Eq. (40) this may be rewritten as:

$$\begin{aligned}&\mathscr{P}_\alpha\varphi_n(-\alpha;\ldots;a_\varepsilon,b_\varepsilon,c_\varepsilon,\ldots)\\ &= p_{n,m_{ab}}\frac{\hbar}{i}\lim_{\Delta\alpha\to 0}\frac{\varphi_n(\alpha-\Delta\alpha;\ldots;a_\varepsilon,b_\varepsilon,-c_\varepsilon,\ldots)-\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,-c_\varepsilon,\ldots)}{\Delta\alpha}\\ &= -p_{n,m_{ab}}\mathscr{P}_\alpha\varphi_n(\alpha;\ldots;a_\varepsilon,b_\varepsilon,-c_\varepsilon,\ldots).\end{aligned} \tag{50}$$

Insertion into the integral expression for the matrix elements and application of the transformation m^{el}_{ab} (Eq. (33)) then finally leads to:

$$\langle 0|\,\mathscr{P}_\alpha\,|n\rangle_{(-\alpha)} = -p^*_{0,m_{ab}}p_{n,m_{ab}}\langle 0|\,\mathscr{P}_\alpha\,|n\rangle_{(\alpha)}. \tag{51}$$

In the same way the other operators and other equivalent α-positions may be treated. In each case — apart from the phase factors — the matrix elements taken for the three other α-values, if compared to the matrix element calculated for the original α-value, do induce a representation of group C_{2v} which is typical for the operator under consideration. The result is listed in Table 5. Since in the expectation values and perturbation sums the phase factors are always paired with their complex conjugates, they are of no further interest and have been neglected in Table 5.

The theoretical expressions, Table 5, and Table 6, in which the symmetry species of the product representations of group C_{2v} are listed may now be used to derive which of the irreducible representations of C_{2v} are generated by the different molecular parameters if they are compared for the four equivalent α-positions (i.e. if the operations $\mathscr{C}^\alpha_{2a}$, m^α_{ab} and m^α_{ac} are applied to them). The result is given in Table 7.

Table 5. Comparison of the electronic matrixelements $\langle 0| \; |n\rangle$ for the four essentially equivalent positions of the top. For any operator the $\langle 0| \; |n\rangle$ matrixelements at the positions $\alpha + \pi$, $-\alpha$ and $-\alpha + \pi$ follow from those calculated for the position α by multiplication with 1 or -1 as given in the Table. Phase factors that will drop out in the perturbation sums and expectation values (see text) are already neglected! In this sence the $\langle 0| \; |n\rangle$-matrixelements generate operator specific irreducible representations of the group C_{2v} whose standard species designations are given in the last column. $\partial^2 V/\partial a\,\partial b$ etc. are the second derivatives of the intramolecular Coulombpotential in direction of the principal inertia axes. They are of importance in molecules which contain quadrupole nuclei such as $H_3C^{14}NO_2$.

Operator	α-positions and transformations of the electron coordinates which transform $\mathscr{H}_{\mathrm{el},\alpha}$ into $\mathscr{H}_{\mathrm{el},\alpha'}$				Symmetry species of group C_{2v} induced by the matrix-elements
	α; I	$\alpha + \pi$; $\mathscr{C}_{2a}^{(\mathrm{el})}$	$-\alpha$; $m_{ab}^{(\mathrm{el})}$	$-\alpha + \pi$; $m_{ac}^{(\mathrm{el})}$	
$\mu_{a\,\mathrm{el}}$, $\mu_{a\,\mathrm{el}}^2$, $\mu_{b\,\mathrm{el}}^2$, $\mu_{c\,\mathrm{el}}^2$ $\frac{\partial^2 V}{\partial a^2}$ $\frac{\partial^2 V}{\partial b^2}$ $\frac{\partial^2 V}{\partial c^2}$ $\sum_{\varepsilon}^{\text{electrons}} (a_\varepsilon^2 + b_\varepsilon^2 + c_\varepsilon^2)$	1	1	1	1	A_1
ℓ_a, $\mathscr{P}_\alpha$, $\frac{\partial^2 V}{\partial b\,\partial c}$	1	1	-1	-1	A_2
ℓ_c, $\mu_{b\,\mathrm{el}}$, $\frac{\partial^2 V}{\partial a\,\partial b}$	1	-1	1	-1	B_1
ℓ_b, $\mu_{c\,\mathrm{el}}$, $\frac{\partial^2 V}{\partial b\,\partial c}$	1	-1	-1	1	B_2

Since the same representation must be generated by the Fourier expansion Eq. (31), the latter must be restricted to either one of the four symmetrized forms, which may be easily obtained by the use of projection operators [26]:

$$A_1\text{-symmetry} \quad f(\alpha) = a_0 + \sum_{n=1}^{\infty} a_{6n} \cos(6n\alpha), \tag{52}$$

$$A_2\text{-symmetry} \quad f(\alpha) = \sum_{n=1}^{\infty} b_{6n} \sin(6n\alpha), \tag{53}$$

$$B_1\text{-symmetry} \quad f(\alpha) = \sum_{n=1}^{\infty} a_{3n} \cos(3n\alpha), \tag{54}$$

$$B_2\text{-symmetry} \quad f(\alpha) = \sum_{n=1}^{\infty} b_{3n} \sin(3n\alpha). \tag{55}$$

Thus for instance the above considerations show, that g_{bb} which according to Table 5 induces the representation A_1, must be expanded as given by Eq. (52), while g_{ab}, which induces the representation B_1, must be expanded according to Eq. (54) etc.

Table 6. Symmetry species of product species of group C_{2v}.

	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

For molecules with a very low barrier to internal rotation one may expect that not only the electronic ground state energy, but also all other molecular parameters show negligible α-dependence. If this were true, only those molecular parameters which generate the unit representation, A_1, should be of practical importance, since only they have a constant, non α-dependent, term. Our experimental data for three isotopic species of Nitromethane, $H_3C^{15}NO_2$, $H_3C^{14}NO_2$, $D_3C^{14}NO_2$ and for $H_3C^{11}BF_2$ indeed rend some credit to the above expectation, since they give no evidence for measurable contributions from non constant terms in the Fourier series.

Appendix

Relations between electronic $\langle n| \; |n'\rangle$-matrix elements involving $\mathscr{P}_\alpha$

During the rearrangement process of the Van Vleck perturbation sums several relations between $\langle n| \; |n'\rangle$-matrixelements were used which may be

Table 7. Comparison of the molecular parameters of the effective rotorsional Hamiltonian for the four "essentially equivalent" α-positions. For positions $\alpha + \pi$, $-\alpha$, and $-\alpha + \pi$ the correct value for the molecular parameters are obtained from their values at position α by multiplication with $+1$ or -1 as given in the Table. In this sense the molecular parameters induce parameter specific irreducible representations of group C_{2v}.

Torsional angle / Molecular parameter	α (I)	$\alpha + \pi$ $(C_{2a}^{(\alpha)})$	$-\alpha$ $(m_{ab}^{(\alpha)})$	$-\alpha + \pi$ $(m_{ac}^{(\alpha)})$	Symmetry species
$g_{aa}, g_{bb}, g_{cc}, g_{a\alpha}$ $\chi_{aa}, \chi_{bb}, \chi_{cc}, \mu_{a\,\mathrm{el}}$ $G_{aa}, G_{bb}, G_{cc}, G_{\alpha\alpha}$	1	1	1	1	A_1
$G_{ab}, G_{b\alpha}$ $g_{ab}, g_{ba}, g_{b\alpha}, g_{\alpha b}, \chi_{ab}, \mu_{b\,\mathrm{el}}$	1	-1	$+1$	-1	B_1
$G_{ac}, G_{c\alpha}$ $g_{ac}, g_{ca}, g_{c\alpha}, g_{\alpha c}, \chi_{ac}, \mu_{c\,\mathrm{el}}$	1	-1	-1	1	B_2
$G_{bc}, g_{bc}, g_{cb}, \chi_{bc}$	1	$+1$	-1	-1	A_2

derived as follows:

$$\langle n|\,\mathscr{P}_\alpha^{(n)}\,|n'\rangle \overset{!}{=} \langle n'|\,\mathscr{P}_\alpha^{(n)}\,|n\rangle^*, \quad n \neq n'. \tag{A.1}$$

The proof is based on the orthogonality of the electronic wavefunctions $\varphi_n(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)$ and $\varphi_{n'}(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)$:

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\varphi_n^*(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots) \cdot \varphi_{n'}(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)\,\mathrm{d}a_1 \ldots \mathrm{d}a_\varepsilon\,\mathrm{d}b_\varepsilon\,\mathrm{d}c_\varepsilon \ldots \mathrm{d}c_N \equiv 0 \quad (\text{all } \alpha).$$

Differentiation of this identity with respect to α, interchanging the sequence of differentiation with respect to α and integration over the electron space, and multiplication with $(\hbar/i)$ directly leads to Equation (A.1).

$$\langle n|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n'\rangle - [\mathscr{P}_a\langle n|\,\ell_a\,|n'\rangle] = \langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle^*. \tag{A.2}$$

The proof of Eq. (A.2) is based on the fact that the operator $\ell_a\mathscr{P}_\alpha$ is hermitian with respect to the complete basis $|n\rangle|j\rangle$ i.e.:

$$\langle j|\langle n|\,\ell_a\mathscr{P}_\alpha\,|n'\rangle\,|j'\rangle = \langle j'|\langle n'|\,\ell_a\mathscr{P}_\alpha\,|n\rangle\,|j\rangle^*.$$

At the right hand side we split $\mathscr{P}_\alpha$ formally into an operator $\mathscr{P}_\alpha^{(n)}$ acting only on the electronic part of the wavefunctions and an operator $\mathscr{P}_\alpha^{(j)}$ acting only on the torsio-rotational part of the wavefunctions. This leads to the following string of equations (note that $\langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle$ and $\langle n'|\,\ell_a\,|n\rangle$ are periodic functions in α):

$$\begin{aligned}
\langle j|\langle n|\,\ell_a\mathscr{P}_\alpha\,|n'\rangle\,|j'\rangle &= \langle j'|\langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle\,|j\rangle^* + \langle j'|\langle n'|\,\ell_a\,|n\rangle\,\mathscr{P}_\alpha^{(j)}\,|j\rangle^* \\
&= \langle j|\langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle^*\,|j'\rangle + \langle j|\,\mathscr{P}_\alpha\langle n|\,\ell_a\,|n'\rangle\,|j'\rangle \\
&= \langle j|\langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle^*\,|j'\rangle \\
&\quad + \overbrace{\langle j|\,[\mathscr{P}_\alpha\langle n|\,\ell_a\,|n'\rangle]\,|j'\rangle + \langle j|\langle n|\,\ell_a\mathscr{P}_\alpha\,|n'\rangle\,|j'\rangle - \langle j|\langle n|\,\ell_a\mathscr{P}_a^{(n)}\,|n'\rangle\,|j'\rangle}
\end{aligned}$$

or

$$\langle j|\langle n|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n'\rangle\,|j'\rangle - \langle j|\,[\mathscr{P}_\alpha\langle n|\,\ell_a\,|n'\rangle]\,|j'\rangle = \langle j|\langle n'|\,\ell_a\mathscr{P}_\alpha^{(n)}\,|n\rangle^*\,|j'\rangle$$

which is equivalent to Equation (A.2).

$$\langle n|\,\mathscr{P}_\alpha^{(n)2}\,|n'\rangle = \langle n'|\,\mathscr{P}_\alpha^{(n)2}\,|n\rangle^* + 2\,[\mathscr{P}_\alpha\langle n|\,\mathscr{P}_\alpha\,|n'\rangle]. \tag{A.3}$$

Again the proof is based on the orthogonality of the electronic wavefunctions:

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\varphi_n^*(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)\,\varphi_{n'}(\alpha; \ldots; a_\varepsilon, b_\varepsilon, c_\varepsilon, \ldots)\,\mathrm{d}a_1 \ldots \mathrm{d}a_\varepsilon\,\mathrm{d}b_\varepsilon\,\mathrm{d}c_\varepsilon \ldots \mathrm{d}c_N \equiv 0 \quad (n \neq n';\ \text{all } \alpha),$$

$$\frac{\partial^2}{\partial\alpha^2}\left(\int\cdots\int \varphi_n^*\,\varphi_{n'}\,\mathrm{d}a_1\ldots\mathrm{d}c_N\right)\equiv 0\,,$$

$$\int\cdots\int \frac{\partial^2}{\partial\alpha^2}\left(\varphi_n^*\,\varphi_{n'}\right)\mathrm{d}a_1\ldots\mathrm{d}c_N\equiv 0\,,$$

$$\int\cdots\int\left[\left(\frac{\partial^2\varphi_n^*}{\partial\alpha^2}\right)\cdot\varphi_{n'}+2\left(\frac{\partial\varphi_n^*}{\partial\alpha}\right)\left(\frac{\partial\varphi_{n'}}{\partial\alpha}\right)+\varphi_n^*\,\frac{\partial^2\varphi_{n'}}{\partial\alpha^2}\right]\mathrm{d}a_1\ldots\mathrm{d}c_N\equiv 0$$

insertion of

$$\int\cdots\int\left(\frac{\partial\varphi_n^*}{\partial\alpha}\right)\cdot\left(\frac{\partial\varphi_{n'}}{\partial\alpha}\right)\mathrm{d}a_1\ldots\mathrm{d}c_N=\frac{\partial}{\partial\alpha}\left(\int\cdots\int\varphi_n^*(\alpha)\,\frac{\partial\varphi_{n'}}{\partial\alpha}\,\mathrm{d}a_1\ldots\mathrm{d}c_N\right)$$
$$-\int\cdots\int\varphi_n^*(\alpha)\,\frac{\partial^2\varphi_{n'}}{\partial\alpha^2}\,\mathrm{d}a_1\ldots\mathrm{d}c_N$$

leads to

$$0=\int\cdots\int\left(\frac{\partial^2\varphi_n^*}{\partial\alpha^2}\right)\cdot\varphi_{n'}\,\mathrm{d}a_1\ldots\mathrm{d}c_N+2\,\frac{\partial}{\partial\alpha}\left(\int\cdots\int\varphi_n^*\left(\frac{\partial\varphi_{n'}}{\partial\alpha}\right)\mathrm{d}a_1\ldots\mathrm{d}c_N\right)$$
$$-\int\cdots\int\varphi_n^*(\alpha)\,\frac{\partial^2\varphi_{n'}}{\partial\alpha^2}\,\mathrm{d}a_1\ldots\mathrm{d}c_N\,.$$

Which after multiplication with $\hbar^2$ is equivalent to Equation (A.3).

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