Contribution of vibrations to the magnetic moment of molecules of the symmetric top type

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A study is made of the magnetic moment induced in molecules of the symmetric top type when degenerate vibrations are excited in them. An expression is derived for the electron contribution to the vibrational g factor. It is shown that the theory of the vibrational magnetic moment developed by Howard, Moss, and Perry is incomplete, since it does not take into account the perturbation of the electron shell by vibrating nuclei.

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1. INTRODUCTION

We shall consider molecules with closed electron shell. It is well known that rotation of a molecule induces a magnetic moment, which consists of nuclear and electron contributions. The nuclear contribution can be readily calculated by means of a model of circular currents corresponding to rotation of positive point charges around a given direction. The rotation of the nuclear core also induces currents in the electron shell, which determine the electron contribution to the magnetic moment. However, the currents in the electron shell are by no means equal to the currents corresponding to rotation of a "frozen" electron shell as a rigid body with the given angular velocity. Usually, these currents are much weaker,[1-4] but in exceptional cases of molecules with neighboring excited states coupled to the ground state by an allowed magnetic dipole transition the currents may be stronger than in the case of rotation of the electron shell as a rigid body.[5-7]

The extent to which the electrons are carried along by the rotating nuclear core is the central problem in the theory of the rotational magnetic moments of molecules. Although the formal solution of this problem in the form of an infinite perturbation sum is well known,[1,8] practical calculations of the electron currents in a rotating molecule (and their contribution to the magnetic moment) present a rather difficult problem which can be solved only approximately. The general analysis of this problem merely tells us that the electrons of the inner shells of atoms having clouds with dimensions small compared with the radii of the circles described by the rotating nuclei are almost completely carried along with the rotation of the nuclear core, whereas the picture of the currents induced in the outer shells of the atoms in the molecule is very complicated.

In their comparatively recent papers Refs. 9 and 10, Howard, Moss, and Perry drew attention to a further source of the magnetic moment of a molecule with closed electron shells. This is the vibrational moment induced by degenerate molecular vibrations. The qualitative picture of the effect is very simple in the case of molecules of the symmetric top type.[11] Let us consider a hypothetical triatomic molecule with the geometry of an equilateral triangle in the equilibrium nuclear configuration. We denote by Q_x and Q_y the real normal coordinates of the doubly degenerate vibration (see Fig. 1). In accordance with Jahn's rule,[10-12] rotations of the form of Q_x and Q_y are not stable when the molecule rotates around the z axis, which passes through the center of mass perpendicular to the plane of the triangle. Indeed, if the vibration Q_x is excited, the Coriolis force induced by the rotation of the molecule will mix it with the Q_y vibration mode. The stable modes are then the complex linear combinations

$$Q_\pm=(Q_x\pm iQ_y)/\sqrt{2}. \tag{1}$$

The coordinates $Q_\pm$ correspond to rotation of each nucleus around its position of equilibrium in a circle whose radius is equal to the vibration amplitude of the given nucleus and with frequency equal to the frequency of the degenerate vibration (see Fig. 2). The instantaneous positions of the neighboring nuclei on their circular orbits are displaced in phase by ±2π/3. With such rotation there is associated an angular momentum, called the vibrational angular momentum of the molecule. Like the rotational angular momentum, it makes a definite contribution to the magnetic moment of the molecule and it has the same order of magnitude (~1 nuclear magneton) as the rotational magnetic moment.

The nuclear contribution to the vibrational magnetic moment of the molecule can be readily calculated, since the motion of the nuclei is determined by the amplitude and frequency of the degenerate vibration. More complicated is the question of the electron contribution to the vibrational magnetic moment, i.e., the magnetic moment resulting from the currents induced in the electron shell of the molecule by excitation of a degenerate Q_+ (or Q_-) vibration. Therefore, the central problem in the theory of the vibrational magnetic moment, as in the case of rotational magnetic moment, is the calculation

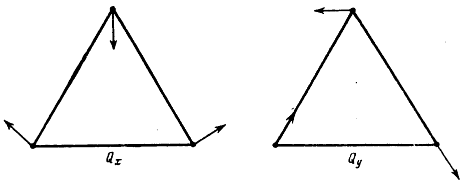

FIG. 1.

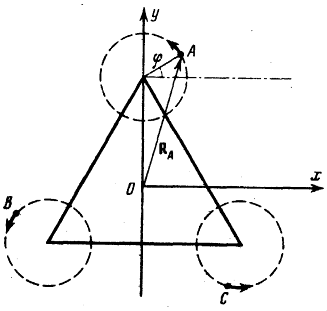

FIG. 2.

of the electron contribution.

Expressions for the electron contribution to the vibrational g factor were obtained in Refs. 9 and 10 on the basis of rather formal calculations; it was found that the electron contribution to the vibrational g factor for molecules which are linear in the equilibrium configuration must be zero, and for molecules of the symmetric top type the contribution must be equal to the electron contribution to the rotational g factor multiplied by the constant of the Coriolis interaction. Unfortunately, both these conclusions of the theory of Howard, Moss, and Perry are incorrect. This is indicated by the fact that the linear molecules HCN and OCS have an appreciable electron contribution to the vibrational g factor.[13] Analysis of the expression obtained by Moss and Perry in the case of symmetric-top molecules shows that it takes into account only the change in the angular velocity of the molecular rotation (for given total angular momentum) in the presence of vibrational angular momentum, i.e., the redistribution of the total angular momentum between the vibrational and rotational degrees of freedom; the direct perturbation of the electrons by the vibrating nuclei and the resulting additional electron currents are not taken into account.

In the present paper, we give a detailed derivation of an expression for the electron contribution to the vibrational g factor of a symmetric-top molecule. A small modification of this derivation also gives an expression for the electron contribution to the vibrational g factor of linear molecules. It will be clear from our treatment of the problem that Refs. 9 and 10 ignore an important term in the molecular Hamiltonian which describes the direct perturbation of the electrons by the nuclei participating in the degenerate vibration.

2. ENERGY OPERATOR AND WAVE FUNCTION OF SYMMETRIC-TOP MOLECULES

We introduce two frames of reference: the molecular coordinate system and the laboratory coordinate system. We attach the Cartesian axes $x_\lambda(\lambda = x,\ y,\ z)$ of the molecular coordinate system to the nuclear core, fixed in the equilibrium configuration. We denote the Eulerian angles that determine the rotation of the molecular frame relative to the laboratory frame by α, β, and γ. The vibrations of the molecules are described by the $3N-6$ vibrational coordinates Q_s (N is the number of nuclei); they determine the displacements of the nuclei from the equilibrium positions and satisfy the Eckart conditions, being orthogonal to the translations and small rotations of the nuclear core as a whole. The positions of the n electrons in the molecular frame are determined by the $3n$ Cartesian coordinates $x_{i\lambda}$ ($x_{i\lambda}$ is the projection of the radius vector of electron i onto the λ axis). We assume that the origin of both frames is at the center of mass of the nuclear core (we shall ignore the small influence of the electrons on the position of the center of mass of the molecules).

With this choice of the coordinates, the molecular state corresponding to total angular momentum $\hbar j$ and projection $\hbar m$ onto the Z axis of the laboratory frame is represented by a wave function of the form[14,15]

$$\Psi_m^j = \sum_{m'=-j}^{j} \Theta_{mm'}^j(\alpha, \beta, \gamma) f_{m'}^j(Q_s, x_{i\lambda}), \tag{2}$$

$$\Theta_{mm'}^j = \left(\frac{2j+1}{8\pi^2}\right)^{1/2} D_{mm'}^j, \tag{3}$$

where $D_{mm'}^j$ are Wigner functions defined in accordance with Ref. 16, and $\hbar m'$ is the projection of the total angular momentum onto the z axis of the molecular frame.

In the adiabatic approximation, the function $f_{m'}^j$ can be represented as the product of a single electron wave function and certain functions $\chi_{m'}^j$, which depend only on the vibrational coordinates, so that the sum (2) takes the form

$$\Psi_m^j \approx \psi_{el}(Q_s|x_{i\lambda}) \sum_{m'=-j}^{j} \Theta_{mm'}^j \chi_{m'j}(Q_s). \tag{4}$$

Here, $\psi_{el}(Q_s|x_{i\lambda})$ is an eigenfunction of the energy operator of the molecule with the operator of the kinetic energy of the nuclei omitted; it depends parametrically on the nuclear coordinates Q_s. In a state with closed electron shells, the function ψ_{el} is real.

It is readily seen that in the adiabatic approximation a closed electron shell makes no contribution to the magnetic moment, currents in the electron shell being absent because the function ψ_{el} is real. The same result can be obtained by calculating the expectation value of the operator of the magnetic moment of the electron shell,

$$\mu = -\mu_B \mathbf{L}/\hbar \tag{5}$$

($\mathbf{L}$ is the angular momentum operator of the electrons, and μ_B is the Bohr magneton), and again bearing in mind that the function ψ_{el} is real. Therefore, the electron contribution to the magnetic moment of a molecule with closed shells is an essentially nonadiabatic effect.[4] In the calculation of this contribution, only the nonadiabatic corrections which lead to the appearance of currents in the electron shell, i.e., the purely imaginary corrections to the electron wave function, are important.

We consider now in more detail the total Hamiltonian of the molecule. In the variables that we have introduced, it has the form (see, for example, Ref. 17)

$$H = T_{el} + T_r + T_v + V(Q_s,\ x_{i\lambda}), \tag{6}$$

where V is the potential energy, and T_{el}, T_r, and T_v are, respectively, the operators of the kinetic energy of the electrons and the rotational and vibrational motion of the nuclei. The two last operators are given by

$$T_r=\sum_\lambda\frac{(\hat{J}_\lambda-\hat{N}_\lambda-\hat{L}_\lambda)^2}{2I_\lambda};\quad T_v=-\frac{\hbar^2}{2M_p}\sum_s\frac{\partial^2}{\partial Q_s^2}. \tag{7}$$

Here, $\hat{J}_\lambda$ is the operator of the angular momentum projection onto the λ axis of the molecular frame; I_λ is the moment of inertia of the nuclear core with respect to the λ axis (we assume that the axes of the molecular coordinate system are directed along the axes of inertia of the equilibrium nuclear configuration, and we ignore the dependence of the moments of inertia on the nuclear coordinates); $\hat{N}_\lambda$ is the operator of the projection of the vibrational angular momentum onto the λ axis. Then the operator **N** is given by

$$\mathbf{N}=-i\hbar\sum_{s,t=1}^{3N-6}\zeta_{st}\left(Q_s\frac{\partial}{\partial Q_t}-Q_t\frac{\partial}{\partial Q_s}\right), \tag{8}$$

where the summation is over all normal coordinates, and the vector ζ_{st}, whose components are c numbers, characterizes the Coriolis coupling of the Q_s and Q_t vibrations. The normalization factor in the kinetic energy T_v of the vibrations in (7) is taken equal to $\hbar^2/2M_p$ (M_p is the proton mass) in order to make the normal coordinates and the displacements corresponding to them in the real space of the same order of magnitude. Then the rms amplitude of the vibrations is $\langle Q_s^2\rangle^{1/2}\sim\varkappa a_0$, where a_0 is the Bohr radius and $\varkappa$ is the Born–Oppenheimer parameter.

We now retain in T_r and T_v only the "vibrational" terms that correspond to the doubly degenerate mode. This is justified since the nondegenerate vibrations influence the vibrational angular momentum only in the higher orders of perturbation theory.[11] For simplicity, we shall assume that we have just a single doubly degenerate vibration. Then on the basis of Jahn's rule[10, 12] we can show that $\hat{N}_x=\hat{N}_y=0$, so that the vibrational angular momentum has a nonvanishing projection only onto the symmetry axis of the molecule:

$$\hat{N}_z=-i\hbar\zeta\left(Q_x\frac{\partial}{\partial Q_y}-Q_y\frac{\partial}{\partial Q_x}\right). \tag{9}$$

For the degenerate vibration, we introduce the two-dimensional polar coordinates

$$Q_x=\rho\cos\varphi;\quad Q_y=\rho\sin\varphi.$$

Then

$$\hat{N}_z=-i\hbar\zeta\partial/\partial\varphi. \tag{10}$$

The wave function in the adiabatic approximation can now be written in the form

$$\Psi_{\text{ad}}=\psi_{el}^{(0)}(\rho,\varphi|x_{i\lambda})\chi(\rho,\varphi)\Theta_{mm'}^{j}(\alpha,\beta,\gamma), \tag{11}$$

where the electron function is the solution of the equation

$$[T_{el}+V(\rho,\varphi,x_{i\lambda})-E_{el,0}(0)-{}^1/_2M_p\omega^2\rho^2]\psi_{el}^{(0)}=0, \tag{12}$$

and the nuclear vibrational–rotational function $\chi\theta_{mm'}^j$ is an eigenfunction of the operator $T_r^{(0)}T_v+\frac{1}{2}M_p\omega^2\rho^2$ (here, $T_r^{(0)}$ is the operator obtained from the operator T_r of the rotational kinetic energy by omitting the terms containing the operator T_r of the electron angular momentum $\hat{L}$). Bearing in mind that

$$T_r^{(0)}+T_v=\frac{\hat{J}^2-J_z^2}{2I_x}+\frac{\left(J_z+i\hbar\zeta\frac{\partial}{\partial\varphi}\right)^2}{2I_z}-\frac{\hbar^2}{2M_p}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right), \tag{13}$$

we obtain the explicit form of the vibrational function χ:

$$\chi=(2\pi)^{-1/2}e^{il\varphi}R_{nl}(\rho), \tag{14}$$

where n is the principal quantum number of the degenerate vibration, the quantum number 1 takes the values $n, n-2, \ldots, -n$, and R_{nl} is the radial part of the eigenfunction of a two-dimensional oscillator in polar coordinates:

$$\left[-\frac{\hbar^2}{2M_p}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{l^2}{\rho^2}\right)+\frac{M_p\omega^2\rho^2}{2}-(n+1)\hbar\omega\right]R_{nl}=0. \tag{15}$$

The expression (11) contains one [and not $2j+1$, like the more general formula (4)] term, since the projection of the angular momentum $\hbar m'$ onto the symmetry axis of the molecule is conserved in the approximation used in the derivation of (11).

3. ALLOWANCE FOR THE NONADIABATIC CORRECTIONS

Applying the operator $H-E_{\text{ad}}$, where H is the exact Hamiltonian of the molecule, to the function (11) of the adiabatic approximation, we find the "discrepancy" $\eta=(H-E_{\text{ad}})\Psi_{\text{ad}}$, which characterizes the adiabatic approximation. The nonadiabatic correction to the wave function in the first order of perturbation theory can be calculated in accordance with

$$\Psi^{(1)}=-(H_{\text{ad}}-E_{\text{ad}})^{-1}(\eta-E^{(1)}\Psi_{\text{ad}}). \tag{16}$$

Here, $E^{(1)}$ is the first-order correction to the energy of the molecule calculated in the adiabatic approximation, and H_{ad} is the energy operator of the molecule modified in such a way that the kinetic energy operator of the nuclei does not act on the electron wave function.

The calculation of the nonadiabatic corrections to the wave function can be simplified by recalling that the real corrections to the electron wave function (11) are unimportant in the calculation of the magnetic moment. We write down only the important, purely imaginary terms in the expression for the function η:

$$\eta=\left[-\frac{(\hat{J}_z-\hat{N}_z)\hat{L}_z}{I_z}-\frac{\hat{J}_x\hat{L}_x+\hat{J}_y\hat{L}_y}{I_x}\right]\Psi_{\text{ad}}$$
$$+\frac{1}{M_p\rho^2}R_{nl}\Theta_{mm'}^{j}\left(-i\hbar\frac{\partial}{\partial\varphi}\frac{e^{il\varphi}}{(2\pi)^{1/2}}\right)\left(-i\hbar\frac{\partial}{\partial\varphi}\psi_{el}^{(0)}(\rho,\varphi|x_{i\lambda})\right). \tag{17}$$

The first two terms are associated with the contribution of the terms in the operator T_r that we ignored in writing down the operator $T_r^{(0)}$. The last term arises because of the action of the kinetic energy operator T_v of the degenerate vibrations of the nuclei on the electron wave function. Using the properties of angular momentum operators, we obtain

$$\eta=\chi(\rho,\varphi)\left[\Theta_{mm'}^{j}\left(-\hbar\frac{m'-\zeta l}{I_z}\hat{L}_z-\frac{il\hbar^2}{M_p\rho^2}\frac{\partial}{\partial\varphi}\right)\psi_{el}^{(0)}\right.$$
$$-\frac{\hbar}{\sqrt{2}I_x}\Theta_{mm'-1}^{j}[(j+m')(j-m'+1)]^{1/2}\hat{L}_{-1}\psi_{el}^{(0)}$$
$$\left.+\frac{\hbar}{\sqrt{2}I_x}\Theta_{mm'+1}^{j}[(j-m')(j+m'+1)]^{1/2}\hat{L}_{+1}\psi_{el}^{(0)}\right], \tag{18}$$

where $\hat{L}_1$ and L_{-1} are the spherical components of the electron angular momentum in the molecular frame:

$$\hat{L}_{\pm 1}=\mp(\hat{L}_x\pm i\hat{L}_y)/\sqrt{2}. \tag{19}$$

The nonadiabatic correction to the molecular wave function responsible for the occurrence of the currents in the electron shell will therefore be

$$\Psi^{(1)}=\chi\big(\overset{j}{\Theta}_{mm'}\psi_{m'}^{(1)}+\overset{j}{\Theta}_{mm'-1}\psi_{m'-1}^{(1)}+\overset{j}{\Theta}_{mm'+1}\psi_{m'+1}^{(1)}\big), \tag{20}$$

where the correction electron functions $\psi_{m'}^{(1)}$, $\psi_{m'\pm 1}^{(1)}$ are solutions of the inhomogeneous equations

$$[T_{el}+V(\rho,\psi,x_{i\lambda})-E_{el}(\rho)]\psi_{m'}^{(1)}=\left(\hbar\frac{m'-\zeta l}{I_z}\hat{L}_z+\frac{il\hbar^2}{M_p\rho^2}\frac{\partial}{\partial\varphi}\right)\psi_{el}^{(0)}, \tag{20a}$$

$$[T_{el}+V(\rho,\varphi,x_{i\lambda})-E_{el}(\rho)]\psi_{m'\pm 1}^{(1)}=\mp\frac{\hbar}{\sqrt{2}\,I_x}[(j\mp m')(j\pm m'+1)]^{1/2}\hat{L}_{\pm 1}\psi_{el}^{(0)}. \tag{20b}$$

4. MAGNETIC MOMENT OF THE ELECTRON SHELL

In a state with fixed projection $\hbar m$ of the total mechanical angular momentum of the molecule onto the Z axis of the laboratory frame, only the Z component of the magnetic moment will be nonzero. The electron contribution to this moment is

$$\mu_Z=-\mu_B\hbar^{-1}\langle\Psi^{(1)}|\hat{L}_Z|\Psi_{\mathrm{ad}}\rangle+\mathrm{c.c.}, \tag{21}$$

where the matrix element is taken with respect to all (electron, vibrational, and rotational) coordinates. We express the operator $\hat{L}_z$ in the laboratory frame in terms of the projections of the electron angular momentum in the molecular frame:

$$\hat{L}_Z=D_{00}^{1}(\alpha\beta\gamma)\hat{L}_z+D_{01}^{1}(\alpha\beta\gamma)\hat{L}_1+D_{0-1}^{1}(\alpha\beta\gamma)\hat{L}_{-1}. \tag{22}$$

We substitute (22) in (21) and integrate over the rotational coordinates with allowance for the structure of the correction function $\Psi^{(1)}$ [see (20)]. Bearing in mind that[18]

$$\int\sin\beta\,d\beta\,d\alpha\,d\gamma\,D_{m_3m_3'}^{j_3*}D_{m_2m_2'}^{j_2}D_{m_1m_1'}^{j_1}=\frac{8\pi^2}{2j_3+1}C_{j_2m_2,j_1m_1}^{j_3m_3}C_{j_2m_2',j_1m_1'}^{j_3m_3'}, \tag{23}$$

and using the explicit expressions for the Clebsch–Gordan coefficients, we obtain

$$\begin{aligned}\mu_Z=-\frac{\mu_Bm}{\hbar[j(j+1)]^{1/2}}\int d\tau_{vib}|\chi(\rho,\varphi)|^2\Big\{&\langle\psi_{m'}^{(1)}|\hat{L}_z|\psi_{el}^{(0)}\rangle\frac{m'}{[j(j+1)]^{1/2}}\\&+\langle\psi_{m'-1}^{(1)}|\hat{L}_{-1}|\psi_{el}^{(0)}\rangle\left[\frac{(j+m')(j-m'+1)}{2j(j+1)}\right]^{1/2}\\&-\langle\psi_{m'+1}^{(1)}|\hat{L}_1|\psi_{el}^{(0)}\rangle\left[\frac{(j-m')(j+m'+1)}{2j(j+1)}\right]^{1/2}\Big\}+\mathrm{c.c.},\end{aligned} \tag{24}$$

where the correction electron functions are defined in accordance with Eqs. (20a) and (20b). Expanding the solutions of these equations with respect to the eigenfunctions of the electron Hamiltonina $T_{el}+V$, and denoting them by $|k\rangle$ ($|0\rangle=\psi_{el}^{(0)}$), we obtain the following expression for the Z projection of the magnetic moment in the laboratory frame:

$$\begin{aligned}\mu_Z=-\frac{\mu_Bm}{\hbar[j(j+1)]^{1/2}}\int d\tau_{vib}|\chi|^2\Big\{\Big[&\frac{\hbar(m'-\zeta l)}{I_z}\sum_{k>0}\frac{|\langle 0|\hat{L}_z|k\rangle|^2}{E_k(\rho,\varphi)-E_0(\rho,\varphi)}\\&+\frac{l\hbar^2}{M_p\rho^2}\sum_{k>0}\frac{\langle k|\hat{L}_z|0\rangle\langle i\partial\psi_{el}^{(0)}/\partial\varphi|k\rangle}{E_k(\rho,\varphi)-E_0(\rho,\varphi)}\Big]\frac{m'}{[j(j+1)]^{1/2}}\\&+\Big[\frac{(j-m')(j+m'+1)}{[2j(j+1)]^{1/2}}\sum_{k>0}\frac{\langle 0|\hat{L}_1^+|k\rangle\langle k|\hat{L}_1|0\rangle}{E_k(\rho,\varphi)-E_0(\rho,\varphi)}\\&+\frac{(j+m')(j-m'+1)}{[2j(j+1)]^{1/2}}\sum_{k>0}\frac{\langle 0|\hat{L}_{-1}^+|k\rangle\langle k|\hat{L}_{-1}|0\rangle}{E_k(\rho,\varphi)-E_0(\rho,\varphi)}\Big]\frac{\hbar}{\sqrt{2}\,I_x}\Big\}+\mathrm{c.c.}\end{aligned} \tag{25}$$

The right-hand side contains matrix elements with the electron functions $|0\rangle$ and $|k\rangle$, which depend on the vibrational coordinates ρ and φ. Once these matrix elements have been calculated, we can set $\rho=0$ in the terms that do not contain $i\partial\psi_{el}^{(0)}/\partial\varphi$ [this approximation has the same accuracy as the assumption used in the energy operator (7) that the moments of inertia are independent of the vibrational coordinates]. In the equilibrium configuration of symmetric-top molecules, we have

$$\sum_{k>0}\frac{\langle 0|\hat{L}_x|k\rangle\langle k|\hat{L}_y|0\rangle}{E_k-E_0}=0;$$

$$\sum_{k>0}\frac{|\langle 0|\hat{L}_x|k\rangle|^2}{E_k-E_0}=\sum_{k>0}\frac{|\langle 0|\hat{L}_y|k\rangle|^2}{E_k-E_0}. \tag{26}$$

As a result, we obtain from (25) the following expression for the electron contribution to the magnetic moment of the molecule in the laboratory frame:

$$\begin{aligned}\mu_Z=\mu_{\mathrm{nuc}}\frac{m}{[j(j+1)]^{1/2}}\Big\{&\frac{m'}{[j(j+1)]^{1/2}}[(m'-\zeta l)g_z^r(e)+lg_z^v(e')]\\&+\frac{j(j+1)-m'^2}{[j(j+1)]^{1/2}}g_x^r(e)\Big\},\end{aligned} \tag{27}$$

where we have introduced the following notation for the g factors:

$$g_z^r(e)=-\frac{2M_p}{m_eI_z}\sum_{k>0}\frac{|\langle 0|\hat{L}_z|k\rangle|^2}{E_k-E_0}; \tag{28a}$$

$$g_x^r(e)=-\frac{2M_p}{m_eI_x}\sum_{k>0}\frac{|\langle 0|\hat{L}_x|k\rangle|^2}{E_k-E_0}; \tag{28b}$$

$$g_z^v(e')=-\frac{\hbar}{m_e}\int d\tau_{vib}|\chi(\rho,\varphi)|^2\frac{1}{\rho^2}\sum_{k>0}\frac{\langle i\partial\psi_{el}^{(0)}/\partial\varphi|k\rangle\langle k|\hat{L}_z|0\rangle}{E_k(\rho,\varphi)-E_0(\rho,\varphi)}+\mathrm{c.c.} \tag{29}$$

If the doubly degenerate vibration is not excited, we have $l=0$, and the expression (27) goes over into the well-known expression for the electron contribution to the rotational magnetic moment of a "rigid" molecule with nuclei fixed in the equilibrium positions (see, for example, the review paper of Ref. 8). When the molecule has vibrational angular momentum, $l\neq 0$. It can be seen from (27) that the presence of vibrational angular momentum leads to two consequences:

a) the contribution associated with the rotational g factor, $g_z^r(e)$, is changed;

b) a new contribution proportional to $g_z^v(e')$ (29) is induced.

Effect a) is trivial. It can be readily deduced from the semiclassical theory of molecular gyromagnetism,[1-3] and it is due to the circumstance that for fixed total angular momentum $\hbar j$ of the molecule the presence of a nonzero vibrational angular momentum leads to a change in the rotational angular momentum, i.e., a change in the angular velocity with which the nuclear core of the molecule rotates. Naturally, this changes the rotational contribution of the electron shell to the magnetic moment of the molecule. Only this effect is taken into account in the theory proposed by Howard, Moss, and Perry.[9,10]

A fundamentally new contribution to the electron magnetic moment of a molecule in which a degenerate vibration is excited is the contribution proportional to $g_z^v(e')$ (29). We shall call it the intrinsic electron contribution to the vibrational g factor. From the semiclassical point of view, $g_z^v(e')$ corresponds to the magnetic moment of the currents induced in the electron shell of the molecule when the nuclei rotate around their equilibrium positions in small circles with the angular frequency of the degenerate vibration.

To estimate the order of magnitude of $g_z^v(e')$, we consider an individual term of the infinite sum in the expression (29):

$$b_k(\rho,\varphi)=\frac{\langle i\partial\psi_{el}^{(0)}/\partial\varphi|k\rangle\langle k|\hat{L}_z|\psi_{el}^{(0)}\rangle+\text{c.c.}}{E_k(\rho,\varphi)-E_0(\rho,\varphi)} \tag{30}$$

and we expand it in a series in powers of ρ. For this, it is convenient to return for the moment to the rectangular normal coordinates Q_x and Q_y. We expand the electron adiabatic wave function of the ground state in powers of the displacements:

$$\psi_{el}^{(0)}(Q_x,Q_y|x_{i\lambda})=\bar{\psi}^{(0)}+\bar{\psi}_xQ_x+\bar{\psi}_yQ_y+{}^1/_2(\bar{\psi}_{xx}Q_x^2+2\bar{\psi}_{xy}Q_xQ_y+\bar{\psi}_{yy}Q_y^2)+\ldots. \tag{31}$$

The bar means that the considered quantities are calculated in the equilibrium nuclear configuration for the electron ground state; the subscripts x, y, xy, etc., denote the derivatives with respect to Q_x and Q_y. For our chosen normalization of the coordinates Q_x and Q_y, these derivatives have zeroth order in the Born–Oppenheimer parameter $\varkappa$. In polar coordinates,

$$\begin{aligned}\psi_{(el)}^{(0)}(\rho,\varphi|x_{i\lambda})=\bar{\psi}^{(0)}&+\rho(\bar{\psi}_x\cos\varphi+\bar{\psi}_y\sin\varphi)\\&+{}^1/_2\rho^2(\bar{\psi}_{xx}\cos^2\varphi+2\bar{\psi}_{xy}\sin\varphi\cos\varphi+\bar{\psi}_{yy}\sin^2\varphi)+\ldots,\end{aligned} \tag{32}$$

$$\partial\psi_{el}^{(0)}/\partial\varphi=\rho(\bar{\psi}_y\cos\varphi-\bar{\psi}_x\sin\varphi)+{}^1/_2\rho^2[\sin2\varphi(\bar{\psi}_{yy}-\bar{\psi}_{xx})+2\bar{\psi}_{xy}\cos2\varphi]+\ldots. \tag{33}$$

Substituting (32) and (33) in (30), we find that the function (30) has the expansion

$$b_k(\rho,\varphi)=\rho\left[-i(\cos\varphi\langle\bar{\psi}_y|\bar{k}\rangle-\sin\varphi\langle\bar{\psi}_x|\bar{k}\rangle)\frac{\langle\bar{k}|\hat{L}_z|\bar{0}\rangle}{\bar{E}_k-\bar{E}_0}+\text{c.c.}\right]+\rho^2F_k(\varphi)+O(\rho^3), \tag{34}$$

where $F_k(\varphi)=\frac{1}{2}\partial^2b_k/\partial\rho^2|_{\rho=0}$ is a periodic function of φ and, in general,

$$\int_0^{2\pi}d\varphi F_k(\varphi)\neq0.$$

Further, substituting (34) in (29) and integrating over the vibrational coordinates with allowance for the fact that $|\chi(\rho,\varphi)|^2$ does not depend on the angular vibrational coordinate φ, we find that the contribution from the term in the square brackets in the expression (34) vanishes. Therefore,

$$g_z^v(e')=-\frac{\hbar}{m_e}\sum_{k>0}\int_0^{2\pi}d\varphi F_k(\varphi)+O\left(\frac{\langle\rho\rangle}{a_0}\right). \tag{35}$$

Since $F_k(\varphi)$ has zeroth order in the small $\varkappa$, the intrinsic electron contribution to the vibrational g factor also has zeroth order in $\varkappa$, i.e., the same order of magnitude with respect to the Born–Oppenheimer parameter as the rotational g factor. It follows that the neglect of (29) is not justified and that this quantity can significantly influence the observed magnetic moment of a molecule.

The above remark can be most readily illustrated for the example of the electrons of inner shells with radii small compared with the amplitude of the degenerate vibration. It is intuitively clear that these electrons are completely carried along with the vibrating nuclei. If the number of inner electrons in each of the atoms is n_0, and the charge of the nucleus of each atom is Z_0, then the intrinsic electron contribution to the vibrational g factor is at least $-(n_0/Z_0)g_z^v(n)$, where $g_z^v(n)$ is the nuclear contribution to the vibrational g factor. The number of inner electrons whose wave functions are hardly perturbed by the formation of the molecule is usually 20–50% of the charge of the nucleus Z_0 (for neutral atoms). Therefore, the quantitative predictions for the vibrational g factor of some specific molecules made in Ref. 10 without allowance for the intrinsic electron contribution (29) to the g factor are definitely incorrect.

The quantum-mechanical expression for the intrinsic electron contribution to the vibrational g factor obtained here is evidently universal. In particular, it also applies to linear molecules (for which, according to the theory of Moss *et al.*, the electron contribution to the vibrational g factor must be absent altogether, which is definitely contradicted by experiment[13]). Indeed, bearing in mind that for a molecule which is linear in the equilibrium nuclear configuration the electron wave function satisfies the euqation

$$i\frac{\partial}{\partial\varphi}\psi_{el}(\rho,\varphi|x_{i\lambda})=-\frac{1}{\hbar}\hat{L}_z\psi_{el}(\rho,\varphi|x_{i\lambda}), \tag{36}$$

(the z axis is directed along the axis of the molecule) and that

$$m'=l,\quad g_z^r(e)=0,$$

we obtain from (27) the following expression for the electron contribution to the vibrational magnetic moment of the linear molecule:

$$\mu_z=\mu_{\text{nuc}}\frac{m}{[j(j+1)]^{1/2}}\left[\frac{l^2}{[j(j+1)]^{1/2}}g_z^v(e')+\frac{j(j+1)-l^2}{[j(j+1)]^{1/2}}g_z^r(e')\right], \tag{37}$$

where the electron contribution to the vibrational g factor is

$$g_z^v(e')=-\frac{2\hbar M_p}{m_e}\int d\tau_{vib}|\chi(\rho,\varphi)|^2\frac{1}{M_p\rho^2}\sum_{k>0}\frac{|\langle0|\hat{L}_z|k\rangle|^2}{E_k(\rho,\varphi)-E_0(\rho,\varphi)} \tag{38}$$

and is equal to the intrinsic electron contribution. The dispersion sum on the right-hand side of (38) can be interpreted as the electron contribution to the vibrational g factor of a slightly bent linear molecule (it would be easy to show that the longitudinal moment of inertia of a deformed molecule is equal to $M_p\rho^2$ in the normalization we have chosen for the coordinates of the doubly degenerate vibration). The expression (38), which contains averaging with respect to the vibrational coordinate ρ, is the quantum-mechanical generalization of the semiclassical model of Hüttner and Morgenstern,[13] in which the vibrational magnetic moment of a linear molecule is interpreted as the rotational magnetic moment of a slightly deformed molecule.

The expression (27) found here for the intrinsic electron contribution to the vibrational magnetic moment of the molecule, and also the expressions for the correction functions (20), which determine the distortion of the the wave functions in the field of nuclei participating in a circularly polarized vibration of the mode Q_+ (or Q_-), can be used in various concrete problems associated with calculating the magnetic properties of molecules with nonzero vibrational moments. In particular, from the form of the correction functions $\psi_{m'}^{(1)}$, $\psi_{m'\pm 1}^{(1)}$ one can determine the currents induced in the electron shell by the vibrations of the nuclear core, and calculate the magnetic fields of the nuclei corresponding to them. This procedure leads to expressions that describe the interaction of the nuclear spin in the molecule with the currents induced in the electron shell by degenerate vibrations with nonzero mechanical angular momentum.

In conclusion, we note a curious connection between the intrinsic electron contribution (29) to the vibrational g factor and the theory of molecular magnetic susceptibility and gyromagnetism. For this, we note that the infinite perturbation sum in the expression (29) can be written in the form

$$\sum_{k>0} \frac{\langle i\partial\psi_{el}^{(0)}/\partial\varphi|k\rangle\langle k|L_z|0\rangle}{E_k(\rho,\varphi)-E_0(\rho,\varphi)} = \frac{1}{\mathscr{H}}\left\langle i\frac{\partial}{\partial\varphi}\psi_{el}^{(0)}\middle| f^{(1)}\right\rangle, \qquad (39)$$

where $f^{(1)}$ is the first-order correction of perturbation theory to the electron wave function of the molecule in the homogeneous magnetic field $\mathscr{H}$ described by the vector potential

$$\mathbf{A}=\mathscr{H}(x\mathbf{e}_y-y\mathbf{e}_x)/2. \qquad (40)$$

Exactly the same correction function $f^{(1)}$ is encountered in the theory of the polarization magnetic susceptibility and in the theory of magnetic phenomena associated with the rotation of molecules having closed electron shells.[4,5,7,19] It can be seen from this that the intrinsic electron contribution to the vibrational magnetic moment can be calculated simultaneously with the electron contribution to the rotational magnetic moment of the molecule.

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