

ON MOLECULAR GYROMAGNETISM

T. K. REBANE

Leningrad State University

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It is shown using the example of a rotating diatomic diamagnetic molecule with identical nuclei that the electronic contribution to the rotational magnetic moment is essentially determined by the nonadiabatic nature of the coupling between the electronic and the nuclear motions.

ALTHOUGH the theory of rotational magnetic moments of diamagnetic molecules has been worked out in considerable detail<sup>[1,2]</sup>, the relation of this theory to the adiabatic approximation has not been discussed in the literature in detail. The object of the present paper is to show that the electronic contribution to the rotational magnetic moment of a diamagnetic molecule is essentially determined by the nonadiabatic nature of the coupling of the motions of the electrons and the nuclei, and also to correct a methodological error made by Mukhtarov<sup>[3]</sup> in discussing the electronic contribution to the magnetic moment of a molecule.

For simplicity we shall restrict ourselves to the case of a diatomic diamagnetic molecule with identical nuclei ( $\alpha = 1, 2$ ). We denote their charges and masses by  $Z_0$  and  $m_0$ . We shall carry out our discussion in the inertial system of the center of mass of the molecule. For a state characterized by zero electron and nuclear spins the magnetic moment operator for the molecule is equal to

$$\hat{\mu}_z = \frac{e}{2c} \left( \frac{Z_0}{m_0} \hat{M}_{z, \text{nuc1}} - \frac{1}{m} \hat{M}_{z, \text{e1}} \right), \quad (1)$$

where  $\hat{M}_{z, \text{nuc1}}$  and  $\hat{M}_{z, \text{e1}}$  are the operators for the z-component of the angular momenta of the nuclei and of the electrons. The total wave function of the molecule has the form

$$\Psi = \Phi(r_j, \theta_j, \varphi_j - \tilde{\varphi}; r_\alpha, \theta_\alpha) \chi(r_\alpha, \theta_\alpha) \exp(i\tilde{M}\tilde{\varphi}), \quad (2)$$

where  $\tilde{\varphi}$  is half the sum of the azimuthal angles for the nuclei. Since the z-component of the total angular momentum is conserved the following relation holds

$$\mu_z = \frac{e}{2c} \left[ \frac{M\hbar Z_0}{m_0} - \left( \frac{1}{m} + \frac{Z_0}{m_0} \right) \int |\chi|^2 d\tau_{\text{nuc1}} \Phi^* \hat{M}_{z, \text{e1}} \Phi d\tau_{\text{e1}} \right]. \quad (3)$$

Substitution of the function (2) into the Schrödinger equation for the stationary states of the molecule yields

$$\begin{aligned} & \Phi \left[ -\frac{\hbar^2}{2m_0} \sum_{\alpha=1}^2 \Delta_\alpha + \frac{Z_0^2 e^2}{R} \right] \chi \exp(i\tilde{M}\tilde{\varphi}) + \chi \exp(i\tilde{M}\tilde{\varphi}) \\ & \times \left[ -\frac{\hbar^2}{2m} \sum_{j=1}^N \Delta_j + e^2 \sum_{j>j'}^n \frac{1}{r_{jj'}} - e^2 Z_0 \sum_{\alpha=1}^2 \sum_{j=1}^N \frac{1}{r_{j\alpha}} \right] \\ & \times \Phi - \frac{\hbar^2}{2m_0} \sum_{\alpha=1}^2 [\chi \exp(i\tilde{M}\tilde{\varphi}) \Delta_\alpha \Phi \\ & + 2(\nabla_\alpha \Phi, \nabla_\alpha \chi \exp(i\tilde{M}\tilde{\varphi}))] = E\Psi, \end{aligned} \quad (4)$$

where E is the total energy of the molecule, and R is the internuclear distance. If we neglect the third term on the left, then from (3) the usual equations of the adiabatic approximation follow:

$$[\hat{H}_{\text{e1}} - E_n(R)] \Phi_n = 0, \quad (5)$$

$$[\hat{H}_{\text{nuc1}} + E_n(R) - E_{n\nu}] \chi_{n\nu} \exp(i\tilde{M}\tilde{\varphi}) = 0 \quad (6)$$

( $\hat{H}_{\text{nuc1}}$  and  $\hat{H}_{\text{e1}}$  denote the operators in the first and the second square brackets in (4), n is the electron state,  $\nu$  is the vibrational-rotational state of the molecule).

However, for the calculation of  $\bar{\mu}_{z, \text{e1}}$  [the second term on the right in (3)] such an approximation is insufficient. Indeed, in the case of a filled electron shell (which is a necessary condition for the molecule to be diamagnetic) Eq. (5) determines the real electron wave function  $\Phi_n$ . This leads to the vanishing of the integral over the electron coordinates in (3):  $\bar{\mu}_{z, \text{e1}}$  vanishes in this approximation. Therefore, it is necessary to make the approximation more precise by utilizing the third term in (4) (the so-called nonadiabatic term). It is essential to take into account only that part of the nonadiabatic term which is responsible for the function  $\Phi$  acquiring an imaginary part:

$$\begin{aligned} & -\frac{iM\hbar^2}{m_0} \chi \exp(i\tilde{M}\tilde{\varphi}) \sum_{\alpha=1}^2 \frac{\partial \Phi}{\partial \varphi_\alpha} / r_\alpha^2 \sin^2 \theta_\alpha \\ & = -\frac{M\hbar}{2m_0} \sum_{\alpha=1}^2 \hat{M}_{z, \text{e1}} \Phi / r_\alpha^2 \sin^2 \theta_\alpha. \end{aligned} \quad (7)$$

With a relative error of the order  $Nm/m_0$  the center of mass of the molecule coincides with the middle of the line connecting the two nuclei. Then from (5) and (7) we obtain the modified equation for the electron wave function  $\Phi'_n$  "perturbed" by the rotation of the molecule:

$$\left[ \hat{H}_{e1} - \frac{4M\hbar}{m_0 R^2 \sin^2 \theta} \hat{M}_{z, e1} - E_{n'}(R) \right] \Phi_{n'} = 0 \quad (8)$$

( $\theta$  is the angle of inclination of the molecular axis to the stationary  $z$  axis). We shall represent the approximate solution of this equation in first order perturbation theory in terms of the set of basis functions  $\Phi_n$  satisfying Eq. (5). Substitution of this approximation for the electron wave function in (3) then yields the formula

$$\mu_{z, e1} = \frac{2Me\hbar}{mm_0c} \int d\tau_{\text{nucl}} \frac{|\chi|^2}{R^2 \sin^2 \theta} \sum_{n' \neq n} \frac{|\langle n' | \hat{M}_{z, e1} | n \rangle|^2}{E_n(R) - E_{n'}(R)}. \quad (9)$$

If  $\hat{M}_{z, e1}$  is the component of the angular momentum of the electrons along the axis lying in the  $z\eta$  plane and perpendicular to the molecular axis  $\eta$ , then the factor  $1/\sin^2 \theta$  in the integrand of (9) cancels and we obtain ( $M_{\eta, e1} \Phi_n = 0$ ).

$$\mu_z = \frac{Me\hbar Z_0}{2m_0c} \times \left[ 1 + \frac{4}{mZ_0} \int d\tau_{\text{nucl}} |\chi|^2 \sum_{n' \neq n} \frac{|\langle n' | \hat{M}_{z, e1} | n \rangle|^2}{E_n(R) - E_{n'}(R)} \frac{1}{R^2} \right]. \quad (10)$$

The relative error in this formula is given by  $Nm/m_0$ . This formula (without taking nuclear vibrations into account) was first derived by Wick<sup>[2]</sup> by a somewhat different method. In cases when the wave functions are known sufficiently accurately

and the perturbation theory series can be summed (or estimated) sufficiently accurately, (10) gives good agreement with experiment (in particular, this holds for the hydrogen molecule).

In conclusion we note that the formula for the electronic contribution to the rotational magnetic moment of the molecule given in the paper by Mukhtarov<sup>[3]</sup> is incorrect. Indeed, for the  $H_2$  molecule a calculation using this formula gives a value for the electronic contribution  $\bar{\mu}_{z, e1} = -3.72$  nuclear magnetons, which exceeds by a factor 30 the experimental value  $-0.11709$  nuclear magnetons<sup>[1]</sup>. The error arises due to the fact that in<sup>[3]</sup> the velocities of the electrons in a rotating molecule (with respect to the rotating system of coordinates) are assumed to be the same as in a molecule with a stationary nuclear core (with respect to a stationary reference system). In particular, the assumption utilized in<sup>[3]</sup>, that in the rotating system of coordinates the average value of the  $z$ -component of the magnetic moment of the electrons is equal to zero, is not valid. These assumptions are unjustified because of the noninertial nature of the rotational reference system.

<sup>1</sup>N. Ramsey, *Molecular Beams*, (Russian Transl.), IIL, 1960, p. 146.

<sup>2</sup>G. C. Wick, *Nuovo cimento* 10, 118 (1933); *Phys. Rev.* 73, 51 (1948).

<sup>3</sup>Ch. K. Mukhtarov, *JETP* 45, 185 (1963), *Soviet Phys. JETP*, 18, 131 (1964).

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