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MOLECULAR GYROMAGNETISM

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The magnetic moments arising during rotation of a molecule as a whole and related to the nuclei and electrons do not compensate each other because of differences in the spatial distribution of the nuclei and electrons. The resulting gyromagnetic moment of the molecule is of the order of $(e/2m_pc)M$ (M is the angular momentum). The paramagnetic susceptibility connected with the gyromagnetic moment does not obey the Curie law and in general does not depend on the temperature. Under stationary conditions this paramagnetism is masked by a stronger diamagnetism. However, the relaxation time of this paramagnetism is related to the time of establishment of rotational equilibrium and in this respect it appreciably differs from diamagnetism.

As is well known, the ground state of the majority of diatomic molecules is the state $^1\Sigma$. This corresponds to the absence of summary electron orbital and spin mechanical and magnetic moments. When the molecule rotates as a whole, the square of its mechanical momentum M is equal to $\hbar^2K(K+1)$; $K = 0, 1, 2, \ldots$ When the molecule rotates, a magnetic moment is produced along with the mechanical one.

An approximate expression for the magnetic moment μ of the molecule (with a relative error $\sim m/m_p$, where m —electron mass, m_p —proton mass) can be written in the following fashion[1]:

$$\boldsymbol{\mu} = -\frac{e}{2c}\left\{\sum_j [\mathbf{r}_j\mathbf{v}_j] - \frac{1}{m_p}\left(\frac{Z_1}{A_1^2}+\frac{Z_2}{A_2^2}\right)\frac{A_1A_2}{A_1+A_2}\mathbf{M}\right\}. \qquad (1)^*$$

Here $\mathbf{r}_j$ and $\mathbf{v}_j$ are the radius vector and the velocity of the j-th electron in the inertial coordinate system with origin at the center of inertia, Z_1 and Z_2 are the atomic numbers and A_1 and A_2 the mass numbers of the nuclei, e is the electron charge, and c is the velocity of light.

To determine the magnetic moment of the molecule it is necessary to find the diagonal matrix element of expression (1), regarding it as an operator. In calculating the matrix elements we use the wave function of the molecule in the adiabatic approximation[2]:

$$\psi_{n,K,M_K} = \Phi_{n,K}(\mathbf{r}_j', R)\,\rho_{n,K}(R)\,P_K^{M_K}(\cos\theta)\,e^{iM_K\varphi}.$$

Here M_K is the quantum number connected with the z component of the total momentum of the molecule, n the set of remaining quantum numbers, which determine the state of the molecule, R is the distance between nuclei, and $\mathbf{r}_j'$ the radius vector of the j-th electron in the system connected with the molecule axis (y' axis). This system has a common origin with the inertial system, but it rotates with angular velocity M/I, where I is the moment of inertia of the molecule.

After multiplying (1) by $|\psi_{n,K,M_K}|^2$ and integrating over the electronic and nuclear coordinates, we obtain

$$\begin{gathered}\langle n, K, M_K|\mu_x|n, K, M_K\rangle = \langle n, K, M_K|\mu_y|n, K, M_K\rangle = 0,\\ \langle n, K, M_K,|\mu_z|n, K, M_K\rangle = -g_K\mu_0M_K,\\ \langle n, K, M_K|\mu^2|n, K, M_K\rangle = g_M^2\mu_0^2K(K+1),\end{gathered} \qquad (2)$$

where

$$g_M = \frac{A_1+A_2}{A_1A_2}\frac{I_e^0}{R_0^2} - \left(\frac{Z_1}{A_1^2}+\frac{Z_2}{A_2^2}\right)\frac{A_1A_2}{A_1+A_2},$$

$$\frac{I_e^0}{R_0^2} = \int\frac{I_e|\rho_{n,K}(R)|^2}{R^2}dR,$$

$$I_e = \sum_j\int(x_j'^2+y_j'^2)|\Phi_{n,K}(\mathbf{r}_j', R)|^2\prod_i dx_i'dy_i'dz_i' \qquad (3)$$

($\mu_0 = e\hbar/2m_pc$ is the nuclear magneton).

Being the proportionality coefficient that relates the magnetic moment measured in nuclear magnetons with the mechanical moment, g_M plays the role of the Lande molecular factor. Since R_0 in (3) is close to the equilibrium value of the internuclear distance, to calculate g_M it is necessary to know only the electronic part of the wave function. Simple estimates show that for a diatomic molecule $g_M \sim 1$. For the hydrogen molecule in the ground state, using a wave function of the Heitler-London type, we obtain $g_M \cong 4$.

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*$[\mathbf{r}_j\mathbf{v}_j] = \mathbf{r}_j \times \mathbf{v}_j$.

In the absence of a magnetic field, each rotational state of the diatomic molecule $2K+1$ is multiply degenerate. On the other hand, if a magnetic field H is applied, the degeneracy is lifted, and each rotational state breaks up into $2K+1$ equidistant levels, with the distance between neighboring levels equal to $g_M\mu_0H$. Thus, in magnetic fields one should observe molecular paramagnetic resonance (of the type of nuclear paramagnetic resonance), but the magnetic field should be sufficiently strong, and the molecules should be able to rotate freely.

As a result of the appearance of the foregoing gyromagnetic moment in molecules in the $^1\Sigma$ state, a gas consisting of such molecules should have paramagnetic properties.

Since the magnetic moment is proportional to the rotational quantum number, the average value of the magnetic moment of the molecule increases with increasing temperature T. The paramagnetic susceptibility χ_p per molecule will in the case $\hbar^2/2IkT \ll 1$ have a value

$$\chi_p = 2g_M^2\mu_0^2 I/3\hbar^2.$$

We see that χ_p does not obey the Curie law and does not depend on the temperature at all.

χ_p is small compared with χ_d —the diamagnetic susceptibility of the molecule, so that $\chi_p/\chi_d \sim -m/m_p$. Thus, under stationary conditions the paramagnetism due to the rotation of the molecules will be masked by the much larger diamagnetism. However, the relaxation time of such a paramagnetism is connected with the time necessary to establish rotational equilibrium, and in this respect the phenomenon considered here differs essentially from diamagnetism.

A magnetic moment of analogous origin can also be related with the rotation of a solid, for example a molecular crystal.

I consider it my pleasant duty to express gratitude to Academician I. V. Obreimov for interest in the work and for much advice.

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[1] L. D. Landau and E. M. Lifshitz, Field Theory (2d. ed.), Addison-Wesley, 1962.

[2] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Addison Wesley, 1958.

Translated by J. G. Adashko
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