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THE ROTATIONAL g FACTOR OF DIATOMIC MOLECULES IN STATE $^1\Sigma^+$ OR 0^+

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I. INTRODUCTION

A. Description of Phenomena

According to a Zeeman effect described as normal, when an appropriate gaseous sample is subjected to an external magnetic field, a spectral line attributed to a pure rotational transition of a typical diatomic molecule appears to split into three components [1–4]. The central component remains at the frequency of a single line observed in the absence of field, and an approximately symmetric displacement of two other lines is linearly proportional to the strength of the externally applied field. The factor of proportionality involves the magnetogyric ratio $\gamma = g_r\mu_N/\hbar$, which is the quotient of magnetic dipolar moment and angular momentum; the rotational g factor g_r (also called the rotational Landé factor) is a signed but dimensionless quantity that depends on nuclear masses and on molecular properties such as the electronic structure, whereas the nuclear magneton $\mu_N = e\hbar/2m_p$ carries units; here the symbols are the charge e and mass m_p of a proton, and $\hbar$, which is Planck's constant h divided by 2π. A typical diatomic molecule has no net angular momentum due to electronic spin or orbital motion which would warrant that it be classified in an electronic state $^1\Sigma^+$ or 0^+, but there may exist net intrinsic nuclear angular momentum of one nucleus or both nuclei that the authors generally ignore in this article. Under these conditions, the total molecular angular momentum is simply that due to rotation of nuclei and their associated electrons about the center of molecular mass. The magnetizability measures the extent of magnetic dipolar moment induced in a rotating molecule by unit density of magnetic flux. As the value of g_r varies only slightly with total angular momentum J (other than nuclear spin) and with vibrational energy, the rotational g factor is an almost characteristic property of a molecule in a particular isotopic variant.

The rotational g factor is of interest, apart from splitting of spectral lines according to the Zeeman effect and molecular magnetizability or the related macroscopic magnetic susceptibility, because this quantity provides information about molecular electric dipolar moments. A free molecule can possess a magnetic dipolar moment; a rotating molecule in general has such a moment apart from any magnetic properties of constituent atomic nuclei. The rotational g factor, which governs the magnitude of magnetic dipolar moment induced with an external magnetic field, provides information through its isotopic dependence about an electric dipolar moment defined with respect to a coordinate system fixed in the molecule. As a result, the sense of the electric moment with respect to the internuclear axis, a property difficult to determine directly using any other traditional experimental method, can thereby be specifically defined. In relation to molecular structure, only on taking into account the rotational g factor can a precise value of the equilibrium rotational parameter B_e that accurately reflects the equilibrium internuclear separation R_e of a diatomic molecular species in a particular isotopic variant be derived from spectral data. An equilibrium internuclear separation R_e^{BO} results from a conventional quantum–chemical calculation in which the electronic problem is solved with clamped nuclei, according to the treatment by Born and Oppenheimer; the latter distance is equivalent to that hypothetically derivable from experimental data pertaining to unattainable conditions of infinitely massive nuclei and temperature 0 K. The difference between distances R_e and R_e^{BO} is attributed to adiabatic effects, which are not truly physical but represent a correction needed to remedy the deficiency of an approximate calculation. Another correction, to take into account that electrons follow imperfectly one or other nucleus in its oscillation and rotation about the center of molecular mass, is attributed to nonadiabatic effects, to which there are rotational and vibrational contributions: the rotational g factor is partly a measure of the rotational contribution. All these aspects of the topic are treated in the present article.

In the absence of a magnetic monopole, the simplest origin of a magnetic dipolar moment, or of a magnetic field associated with such a dipolar moment, is rotating charge, or an electric current in a loop. Hence, a model for a molecular magnetic dipole arising on rotation is either an electric charge located apart from a center of mass about which rotation occurs, or an electric dipole the two poles of which are *not* equidistant from the center of mass; the latter condition applies if the masses of two atomic nuclei at which the poles are supposed to be located are unequal. As diatomic molecules of most species possess a finite electric dipolar moment with respect to a nuclear frame, this condition makes possible a common mechanism according to which one can envisage a molecular magnetic dipole to arise; thus, the splitting of spectral lines on application of an external magnetic field to a gaseous sample is consistent with generation of molecular magnetic dipoles that interact with that applied field. That also molecules such as $^1H_2$ lacking a permanent electric dipole exhibit a rotational magnetic moment indicates that this property originates not only from such a rotating electric dipole, but that this physical behavior is associated conventionally with nonadiabatic effects [5], as mentioned above.

Both experiments and calculations designed to evaluate a rotational g factor involve significant difficulty. Spectral measurements of the Stark effect on subjecting a sample to an electric field have been commonly undertaken much more frequently than measurements of the Zeeman effect conventionally applied to provide accurate magnitudes of g_r, and developments in microwave spectrometry with samples in gaseous jets that greatly enhance sensitivity appear to preclude measurement of both such effects. Unlike a calculation of electric dipolar moment that is a simple expectation value of the electronic ground state, calculation of an electronic contribution to a rotational g factor of the same state in principle requires a knowledge of all excited states; hence this property is described as being of second order, because it depends on corrections of first order to the wave function of the ground state. A calculation of a g factor using these expressions that involve sums over states is impracticable for all but the simplest molecules; thus, other methods are devised to serve that purpose.

In this article we present a critical assessment of the current state of knowledge concerning the rotational g factor, including a survey of experimental [6] and theoretical or computational [7] methods for its evaluation for particular diatomic molecular species and consideration of its association with other chemical and physical properties of gaseous chemical samples. Known values of the rotational g factor for diatomic molecular species in an electronic state of symmetry $^1\Sigma^+$ or 0^+ are compiled in an appendix. Comment on rotational g factors of molecules in other electronic states is provided.

B. Chronicle of Origins of Rotational g Factor

The first report of a diatomic rotational g factor resulted from measurements on *para*-$^1H_2$ in a molecular beam undergoing deflection in a magnetic field [8,9]; a rough value $0.8 < |g_r| < 0.9$ for $^1H_2$ [9] was inconsistent with a prediction $g_r = -2.72$ [10] or $g_r = -3$ [8,11] of a simple theory according to which electrons rotate with nuclei as a rigid distribution of charge. A revised treatment [11–14] which takes into account perturbation of electronic motion by rotation successfully accounts for the observed magnitude and shows the relation of the rotational g factor to magnetizability. A refined experiment with a molecular beam and magnetic resonance [11] yielded both improved precision of magnitude and a sign, $g_r = +0.8787$ for $^1H_2$; this value is near the maximum positive value, $g_r = 1$, that would occur if electrons made no contribution to molecular magnetic moment [15].

The first observation of a Zeeman effect on a pure rotational transition was made on samples of gaseous ammonia ($^{14}N^1H_3$ and $^{15}N^1H_3$) in its inversion spectrum [16], and later for the diatomic molecule $^{12}C^{16}O$ [17]. After these phenomena pertaining to microwave spectra were discovered, theories of the rotational g factor of symmetric–rotor [18] or general molecules [19] soon ensued.

C. Definition of Magnetic Quantities

1. *Magnetizability*

We relate the rotational g factor to other magnetic properties, all relevant quantities consistent with SI convention [20]. As magnetizability and the rotational g factor are closely connected, begin by considering the former quantity.

When a dilute gaseous sample consisting of freely rotating molecules is subjected to an external magnetic field, each molecule acquires an induced magnetic dipolar moment $\vec{m}_{in}$ proportional to the density $\vec{B}$ of magnetic flux inside the sample:

$$\vec{m}_{in} = \xi \vec{B} \tag{1.1}$$

the factor of proportionality is a tensorial quantity called molecular magnetizability ξ. The magnetic-flux density enters the electronic Hamiltonian in the form of its vector potential $\vec{A}$, which for a static and spatially uniform magnetic field $\vec{H}$ is given as

$$\vec{A} = \sum_i \vec{A}_i = \frac{1}{2} \sum_i \vec{B} \times (\vec{r}_i - \vec{R}_o) \tag{1.2}$$

in which $\vec{R}_o$ is an arbitrary origin of gauge and the summation runs over all electrons i with position vector $\vec{r}_i$. The electronic Hamiltonian is obtained on substituting, for the operator $\vec{p}_i$ for linear momentum of electron i, the gauge-invariant operator $\vec{\pi}_i$ for momentum,

$$\vec{\pi}_i = \vec{p}_i + e\vec{A}_i \tag{1.3}$$

whereby

$$H = \frac{1}{2m_e}\sum_i \vec{\pi}_i^2 + V = \frac{1}{2m_e}\sum_i (\vec{p}_i^{\,2} + 2e\vec{A}_i \cdot \vec{p}_i + e^2\vec{A}_i \cdot \vec{A}_i) + V \tag{1.4}$$

We employ a fact that $\vec{A}_i$ fulfil the Coulomb gauge ($\vec{\nabla} \cdot \vec{A}_i = 0$). V is an operator for potential energy for interactions between electron and nucleus and between electron and electron, and is possibly due to an external electric field. Insertion of Eq. (1.2) gives

$$\begin{aligned} H &= \frac{1}{2m_e}\sum_i \vec{p}_i^{\,2} + V + \frac{e}{2m_e}\sum_i \vec{B} \cdot (\vec{r}_i - \vec{R}_o) \times \vec{p}_i \\ &\quad + \frac{e^2}{8m_e}\sum_i (\vec{B} \times (\vec{r}_i - \vec{R}_o)) \cdot (\vec{B} \times (\vec{r}_i - \vec{R}_o)) \\ &= \frac{1}{2m_e}\sum_i \vec{p}_i^{\,2} + V + \frac{e}{2m_e}\sum_i \vec{B} \cdot \vec{l}_i(\vec{R}_o) \\ &\quad + \frac{e^2}{8m_e}\sum_i \sum_{\alpha\beta} B_\alpha \{(\vec{r}_i - \vec{R}_o)^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{o,\alpha})(r_{i,\beta} - R_{o,\beta})\} B_\beta \end{aligned} \tag{1.5}$$

The indices α, β denote, both here and in the following, Cartesian components x, y, z; $\vec{l}_i(\vec{R}_o)$ is an operator for electronic angular momentum of electron i defined with respect to the gauge origin $\vec{R}_o$.

Using Rayleigh–Schrödinger perturbation theory, one obtains a correction to unperturbed wave functions $\Psi_0^{(0)}$ from the applied field to first order:

$$\Psi_0^{(1)} = \sum_{n \neq 0} \frac{\langle \Psi_n^{(0)} \mid \frac{e}{2m_e}\sum_i \vec{B} \cdot \vec{l}_i(\vec{R}_o) \mid \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \Psi_n^{(0)} \tag{1.6}$$

The induced magnetic dipolar moment $\vec{m}_{in}$ is then obtained from the density $\vec{j}_{in}$ of induced current as

$$\vec{m}_{in} = \frac{1}{2}\int (\vec{r} - \vec{R}_o) \times \vec{j}_{in}(\vec{r}) d\vec{r} \tag{1.7}$$

which to first order is

$$\begin{aligned}\vec{j}_{in}(\vec{r}_1) = N \int \Bigg\{ & -\frac{e^2}{m_e}\Psi_0^{(0)*}\vec{A}\Psi_0^{(0)} \\ & -\frac{e}{2m_e}\Bigg[\Psi_0^{(0)*}\Bigg(\sum_i \vec{p}_i\Bigg)\Psi_0^{(1)} + \Psi_0^{(1)*}\Bigg(\sum_i \vec{p}_i\Bigg)\Psi_0^{(0)} \\ & -\Psi_0^{(0)}\Bigg(\sum_i \vec{p}_i\Bigg)\Psi_0^{(1)*} - \Psi_0^{(1)}\Bigg(\sum_i \vec{p}_i\Bigg)\Psi_0^{(0)*}\Bigg]\Bigg\} ds_1 d\vec{x}_2 \cdots d\vec{x}_N \end{aligned} \tag{1.8}$$

Here $\vec{x}_i = \vec{r}_i s_i$ denotes a combined spatial and spin variable for electron i. Insertion of the first-order wave function $\Psi_0^{(1)}$, Eq. (1.6), into Eq. (1.8), performing the integration in Eq. (1.7) and comparing the result with Eq. (1.1) yields an expression [21] according to second-order perturbation theory for magnetizability with its diamagnetic and paramagnetic contributions:

$$\begin{aligned}\xi_{\alpha\beta}(\vec{R}_o) &= \xi^d_{\alpha\beta}(\vec{R}_o) + \xi^p_{\alpha\beta}(\vec{R}_o) \\ &= -\frac{e^2}{4m_e}\left\langle \Psi_0^{(0)} \middle| \sum_i ((\vec{r}_i - \vec{R}_o)^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{o,\alpha}) \right. \\ &\quad \left. \times (r_{i,\beta} - R_{o,\beta})) \middle| \Psi_0^{(0)} \right\rangle - \frac{e^2}{4m_e^2}\sum_{n\neq 0} \cdot \\ &\quad \times \left(\frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_n^{(0)}\rangle\langle \Psi_n^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_o) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \right. \\ &\quad \left. + \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_o) \mid \Psi_n^{(0)}\rangle\langle \Psi_n^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \right) \end{aligned} \tag{1.9}$$

The effect of magnetic field on a sample of molecules is described macroscopically in terms of magnetization $\vec{M}$ of the sample. This quantity is proportional to strength $\vec{H}$ of magnetic field

$$\vec{M} = \chi\vec{H} \tag{1.10}$$

in which a factor of proportionality is another tensorial quantity called magnetic susceptibility. For molecules lacking angular momentum due both to net electronic orbital motion and to spin, the magnetization of a bulk sample of concentration $\mathcal{N}$ independent molecules per unit volume depends only on induced magnetic moments:

$$\vec{M} = \mathcal{N}\vec{m}_{in} \tag{1.11}$$

From a relation

$$\vec{B} = \vec{B}_0 + \mu_0\vec{M} = \mu_0(\vec{H} + \vec{M}) = \mu_0(1 + \boldsymbol{\chi})\vec{H} \tag{1.12}$$

and Eqs. (1.1), (1.10), and (1.11), macroscopic magnetic susceptibility becomes related to molecular magnetizability,

$$\boldsymbol{\chi}(1 + \boldsymbol{\chi})^{-1} = \mathcal{N}\mu_0\boldsymbol{\xi} \tag{1.13}$$

in which μ_0 and $\vec{B}_0$ are respectively magnetic permeability and density of magnetic flux, both of free space. For isotropic samples such as molecules in dilute gaseous and nonviscous liquid states of aggregation, only traces χ and ξ of tensorial quantities $\boldsymbol{\chi}$ and $\boldsymbol{\xi}$ are of interest. Under these conditions applicable to a gaseous sample and under a (standard) restriction that magnetization is small ($|\chi| \ll 1$),

$$\chi = \mathcal{N}\mu_0\xi \tag{1.14}$$

which thus establishes a relationship between macroscopic magnetic susceptibility and microscopic magnetizability.

2. *Rotational g Factor*

We proceed to examine the definition of the rotational g factor; when a molecule in an electronic state $^1\Sigma^+$ or 0^+ is not rotating, it has no net magnetic dipolar moment, apart from nuclear properties. When a molecule rotates with angular momentum $\vec{J}$ (carrying units J s), it acquires a net rotational magnetic moment

$$\vec{m}_r = \frac{\mu_N}{\hbar}\boldsymbol{g}_r\vec{J} \tag{1.15}$$

in which $\boldsymbol{g}_r$ is the rotational g tensor, the trace of which is the rotational g factor, g_r. To the latter there are nuclear and electronic contributions. Nuclei k with position vectors $\vec{R}_k$ and atomic numbers Z_k are generally treated classically; their contribution to rotational magnetic moment is ascertained on considering the motion of charged particles:

$$m^{n}_{r,\alpha} = \frac{\mu_N m_p}{\hbar}\sum_{\beta}\sum_{k} Z_k \times \left((\vec{R}_k - \vec{R}_{\mathrm{CM}})^2 \delta_{\alpha\beta} - (R_{k,\alpha} - R_{\mathrm{CM},\alpha})(R_{k,\beta} - R_{\mathrm{CM},\beta})\right)\frac{J_\beta}{I_\beta} \tag{1.16}$$

Here $\boldsymbol{I}$ denotes a tensor for moment of inertia that contains nuclear masses; $\vec{R}_{\mathrm{CM}}$ is the position vector of the center of nuclear mass. The nuclear masses in $\boldsymbol{I}$ are generally approximated with atomic masses and $\vec{R}_{\mathrm{CM}}$ is approximated with the center of atomic masses. The contribution of electrons to magnetic moment is treated according to wave mechanics on taking expectation values of appropriate electronic wave functions. A rigid distribution of electrons rotating with nuclei produces a contribution analogous to Eq. (1.16), i.e.,

$$m^{e,\mathrm{rigid}}_{r,\alpha} = -\frac{\mu_N m_p}{\hbar}\sum_{\beta}\left\langle\Psi_n^{(0)}\middle|\sum_{i}\left((\vec{r}_i - \vec{R}_{\mathrm{CM}})^2\delta_{\alpha\beta} - (r_{i,\alpha} - R_{\mathrm{CM},\alpha}) \times (r_{i,\beta} - R_{\mathrm{CM},\beta})\right)\middle|\Psi_n^{(0)}\right\rangle\frac{J_\beta}{I_\beta} \tag{1.17}$$

Coupling between electronic motion and molecular rotation, signifying failure of the Born–Oppenheimer approximation (see Section I.D), introduces a term $\sum_i \vec{l}_i(\vec{R}_{\mathrm{CM}}) \cdot \vec{J}$ into the electronic Hamiltonian. Treating it as a perturbation generates additional contributions to $m^{e}_{r,\alpha}$. Within an alternative approach [12,13] consistent with our exposition of magnetizability, rotation according to Larmor's theorem produces a density of magnetic flux

$$\vec{B}^{\,r} = -\frac{2m_e}{e}\vec{J}\boldsymbol{I}^{-1} \tag{1.18}$$

for which one defines a vectorial potential

$$\vec{A}^r = \sum_i \vec{A}^r_i = -\frac{m_e}{e}\sum_i \vec{J} \times (\vec{r}_i - \vec{R}_{\mathrm{CM}})\boldsymbol{I}^{-1} \tag{1.19}$$

Analogous to external magnetic-flux density in Eq. (1.6), a correction to the wave function

$$\Psi_0^{(1)} = \sum_{n\neq 0}\frac{\langle\Psi_n^{(0)}|\sum_i \vec{l}_i(\vec{R}_{\mathrm{CM}})\cdot\vec{J}\boldsymbol{I}^{-1}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\Psi_n^{(0)} \tag{1.20}$$

arises in first order; an induced current density arises analogously. The induced electronic contribution to rotational magnetic moment is thus

$$
\begin{aligned}
m_{r,\alpha}^{e,ind} &= \frac{\mu_N m_p}{\hbar} \sum_{\beta} \frac{J_\beta}{I_\beta} \\
&\left\{ \frac{1}{m_e} \sum_{n \neq 0} \left(\frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\mathrm{CM}}) \mid \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right. \right. \\
&\qquad \left. + \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\mathrm{CM}}) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right) \\
&\quad + \left\langle \Psi_0^{(0)} \middle| \sum_i ((\vec{r}_i - \vec{R}_o) \cdot (\vec{r}_i - \vec{R}_{\mathrm{CM}}) \delta_{\alpha\beta} \right. \\
&\quad \left. \left. - (r_{i,\alpha} - R_{\mathrm{CM},\alpha})(r_{i,\beta} - R_{o,\beta})) \middle| \Psi_0^{(0)} \right\rangle \right\} \qquad (1.21)
\end{aligned}
$$

Combining this with a contribution from the rigid density of electrons, Eq. (1.17), yields

$$
\begin{aligned}
m_{r,\alpha}^{e} &= \frac{\mu_N m_p}{\hbar} \sum_{\beta} \frac{J_\beta}{I_\beta} \\
&\times \left\{ \frac{1}{m_e} \sum_{n \neq 0} \left(\frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\mathrm{CM}}) \mid \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right. \right. \\
&\qquad \left. + \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\mathrm{CM}}) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_o) \mid \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right) \\
&\quad - \left\langle \Psi_0^{(0)} \middle| \sum_i (\vec{R}_o - \vec{R}_{\mathrm{CM}}) \cdot (\vec{r}_i - \vec{R}_{\mathrm{CM}}) \delta_{\alpha\beta} \right. \\
&\quad \left. \left. - (r_{i,\alpha} - R_{\mathrm{CM},\alpha})(R_{o,\beta} - R_{\mathrm{CM},\beta})) \middle| \Psi_0^{(0)} \right\rangle \right\} \qquad (1.22)
\end{aligned}
$$

This equation is the final expression for magnetic moment in a classical form comprising two terms, one paramagnetic term—a sum over excited states, and the other diamagnetic—an average over the ground state. Noting that

$$
\begin{aligned}
&\left\langle \Psi_0^{(0)} \middle| \sum_i ((\vec{r}_i - \vec{R}_{\mathrm{CM}}) \cdot (\vec{R}_o - \vec{R}_{\mathrm{CM}}) \delta_{\alpha\beta} - (r_{i,\alpha} - R_{\mathrm{CM},\alpha})(R_{o,\beta} - R_{\mathrm{CM},\beta})) \middle| \Psi_0^{(0)} \right\rangle \\
&= \frac{1}{\imath\hbar} \left\langle \Psi_0^{(0)} \middle| \sum_i [((\vec{R}_o - \vec{R}_{\mathrm{CM}}) \times \vec{r}_i)_\alpha, l_{i,\beta}(R_{\mathrm{CM}})] \Psi_0^{(0)} \right\rangle, \qquad (1.23)
\end{aligned}
$$

inserting the resolution of the identity $1=\sum_n |\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|$, and using the hypervirial relation $\langle\Psi_n^{(0)} \mid \sum_i \vec{p}_i \mid \Psi_0^{(0)}\rangle = \frac{m_e}{\imath\hbar}(E_0^{(0)} - E_n^{(0)})$ $\langle\Psi_n^{(0)} \mid \sum_i \vec{r}_i \mid \Psi_0^{(0)}\rangle$, one expresses the diamagnetic contribution alternatively as a sum over excited states,

$$\begin{aligned}&\left\langle\Psi_0^{(0)}\middle|\sum_i((\vec{r}_i - \vec{R}_{\text{CM}})(\vec{R}_o - \vec{R}_{\text{CM}})\delta_{\alpha\beta} - (r_{i,\alpha} - R_{\text{CM},\alpha})(R_{o,\beta} - R_{\text{CM},\beta}))\middle|\Psi_0^{(0)}\right\rangle \\ &\quad = -\frac{1}{m_e}\sum_{n\neq 0}\left(\frac{\langle\Psi_0^{(0)} \mid \sum_i((\vec{R}_o - \vec{R}_{\text{CM}}) \times \vec{p}_i)_\alpha \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\text{CM}}) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right. \\ &\qquad \left. + \frac{\langle\Psi_0^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\text{CM}}) \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \sum_i((\vec{R}_o - \vec{R}_{\text{CM}}) \times \vec{p}_i)_\alpha \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right)\end{aligned} \tag{1.24}$$

Combination of two terms for sums over excited states in Eqs. (1.22) and (1.24) with a nuclear contribution in Eq. (1.16) and comparison with Eq. (1.15) yields an expression for components of the rotational g tensor [19]:

$$\begin{aligned}g_{r,\alpha\beta} &= \frac{m_p}{I_\beta}\sum_K Z_K((\vec{R}_K - \vec{R}_{\text{CM}})^2\delta_{\alpha\beta} - (R_{K,\alpha} - \vec{R}_{\text{CM},\alpha})(R_{K,\beta} - \vec{R}_{\text{CM},\beta})) \\ &\quad + \frac{m_p}{m_e I_\beta}\sum_{n\neq 0}\left(\frac{\langle\Psi_0^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_{\text{CM}}) \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\text{CM}}) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right. \\ &\qquad \left. + \frac{\langle\Psi_0^{(0)} \mid \sum_i l_{i,\beta}(\vec{R}_{\text{CM}}) \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \sum_i l_{i,\alpha}(\vec{R}_{\text{CM}}) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right)\end{aligned} \tag{1.25}$$

The electronic contribution $g_{r,\alpha\beta}^e$ is related to the paramagnetic contribution $\xi_{\alpha\beta}^p$ to magnetizability [Eq. (1.9)], evaluated with the center of mass as gauge origin:

$$g_{r,\alpha\beta}^e = -\frac{4m_p m_e}{e^2 I_\beta}\xi_{\alpha\beta}^p(\vec{R}_{\text{CM}}) \tag{1.26}$$

For a linear molecule with nuclei along the z-axis, $J_z = 0$ and $g_{r,zz} = 0$; from symmetry $g_{r,xx} = g_{r,yy}$, and the g tensor becomes reduced to a single parameter $g_r = g_{r,xx} = g_{r,yy}$, which would not vary with J for a molecule rotating rigidly. For a diatomic molecule AB containing nucleus A of protonic number Z_a and nuclear mass m_a along the z-axis at $z_a = |\vec{R}_a - \vec{R}_{\rm CM}|$ and nucleus B with protonic number Z_b and nuclear mass m_b at $z_b = |\vec{R}_b - \vec{R}_{\rm CM}|$, the nuclear contribution becomes

$$g_r^n = \frac{m_p}{I}\left(Z_a z_a^2 + Z_b z_b^2\right) = m_p \frac{Z_a m_b^2 + Z_b m_a^2}{m_a m_b (m_a + m_b)} \tag{1.27}$$

in which the moment of inertia is $I = \mu_n R^2 = \frac{m_a m_b}{m_a + m_b}(\vec{R}_a - \vec{R}_b)^2$. As already mentioned, the nuclear reduced mass μ_n is commonly approximated with the atomic reduced mass $\mu_n \approx \mu = M_a M_b / (M_a + M_b)$. The second form of g_r^n shows that the nuclear contribution is independent of internuclear distance and is thus constant for a particular molecular species in all its electronic states. For a molecule with two identical nuclei ($Z_a = Z_b$, $m_a = m_b$), the sum of Eq. (1.27) and the appropriate component of Eq. (1.26) simplifies to

$$\xi_\perp^p = \left(\frac{1}{2} Z_a - \frac{\mu_n}{m_p} g_r\right) \frac{e^2 R_e^2}{4 m_e} \tag{1.28}$$

The total perpendicular component of magnetizability is thus evaluable from the rotational g factor and a computed diamagnetic contribution $\xi_\perp^d(\vec{R}_{\rm CM})$,

$$\xi_\perp(\vec{R}_{\rm CM}) = \xi_\perp^d(\vec{R}_{\rm CM}) - \frac{e^2 I}{4 m_e m_p} g_r^e \tag{1.29}$$

of which so called direct experimental observation is impracticable. Many magnetizabilities experimental have been obtained with this relation even though, rigorously, only g_r is measured experimentally.

So far the magnetizability and rotational g factor are discussed only in a context of induced magnetic dipolar moments. To establish their relation to the electronic energy $E(\vec{B})$ of a rotating molecule in a magnetic field of flux density $\vec{B}$, one integrates an expression for interaction of a magnetic dipolar moment with a differential density of magnetic flux:

$$E(\vec{B}) = E_0 + \int (\vec{m} + \vec{m}_{in}) \cdot d\vec{B} \tag{1.30}$$

As the induced magnetic moment is given by Eqs. (1.1) and (1.15), one thus obtains

$$E(\vec{B}) = E_0 - \vec{m} \cdot \vec{B} - \frac{\mu_N}{\hbar} \vec{B} g_r \vec{J} - \frac{1}{2} \vec{B} \xi \vec{B} \tag{1.31}$$

3. *Relation Between Rotational g Factor and Electric Dipolar Moment*

We derive a relation between the rotational g factor of a diatomic molecule and its electric dipolar moment [22]. Choosing the position vector of a nucleus, e.g., $\vec{R}_a$ instead of $\vec{R}_{\mathrm{CM}}$, as an origin in the expression, Eq. (1.25), for the rotational g factor, one finds

$$g_r^a(R) = \frac{m_p}{\mu_n} Z_b + \frac{2m_p}{m_e \mu_n R^2} \sum_{n \neq 0} \times \frac{\langle \Psi_0^{(0)} \,|\, \sum_i l_{i,x}(\vec{R}_a) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \sum_i l_{i,x}(\vec{R}_a) \,|\, \Psi_0^{(0)} \rangle}{E_0 - E_n} \tag{1.32}$$

This result is essentially the rotational g factor for a molecule AB that rotates hypothetically around nucleus A. Correspondingly, with nucleus B as origin one obtains

$$g_r^b(R) = \frac{m_p}{\mu_n} Z_a + \frac{2m_p}{m_e \mu_n R^2} \sum_{n \neq 0} \times \frac{\langle \Psi_0^{(0)} \,|\, \sum_i l_{i,x}(\vec{R}_b) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \sum_i l_{i,x}(\vec{R}_b) \,|\, \Psi_0^{(0)} \rangle}{E_0 - E_n} \tag{1.33}$$

The arithmetical average of $g_r^a(R)$ and $g_r^b(R)$, called g_r^{irr} for reasons to be discussed, is then

$$g_r^{irr}(R) = \frac{1}{2}\left(g_r^a(R) + g_r^b(R)\right) \tag{1.34}$$

$$\begin{aligned} &= \frac{m_p}{\mu_n}\left(\frac{Z_a + Z_b}{2} + \frac{1}{m_e R^2} \right. \\ &\quad \times \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}_a) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}_a) \mid \Psi_0^{(0)} \rangle}{E_0 - E_n} \\ &\quad \left. + \frac{1}{m_e R^2} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}_b) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}_b) \mid \Psi_0^{(0)} \rangle}{E_0 - E_n} \right) \end{aligned} \tag{1.35}$$

This equation is rewritten as

$$\begin{aligned}
g_r^{irr}(R) = {} & \frac{m_p}{\mu_n}\frac{Z_a+Z_b}{2} + \frac{m_p}{m_e\mu_n R^2} \\
& \times \Bigg(2\sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{CM}}) \mid \Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{CM}}) \mid \Psi_0^{(0)}\rangle}{E_0 - E_n} \\
& - \{(R_{\mathrm{CM},z} - R_{a,z}) + (R_{\mathrm{CM},z} - R_{b,z})\} \\
& \times \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i p_{i,y} \mid \Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{CM}}) \mid \Psi_0^{(0)}\rangle}{E_0 - E_n} \\
& - \{(R_{\mathrm{CM},z} - R_{a,z}) + (R_{\mathrm{CM},z} - R_{b,z})\} \\
& \times \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{CM}}) \mid \Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} \mid \sum_i p_{i,y} \mid \Psi_0^{(0)}\rangle}{E_0 - E_n} \\
& + \{(R_{\mathrm{CM},z} - R_{a,z})^2 + (R_{\mathrm{CM},z} - R_{b,z})^2\} \\
& \times \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i p_{i,y} \mid \Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} \mid \sum_i p_{i,y} \mid \Psi_0^{(0)}\rangle}{E_0 - E_n} \Bigg)
\end{aligned} \tag{1.36}$$

The second term is the electronic contribution to the rotational g factor, and the latter three terms can be reformulated, again using hypervirial relations and resolution of an identity, to produce

$$\begin{aligned}
g_r^{irr}(R) = {} & g_r(R) - \frac{m_p}{\mu_n R^2}(Z_a(R_{a,z} - R_{\mathrm{CM},z})^2 + Z_b(R_{b,z} - R_{\mathrm{CM},z})^2) \\
& + \frac{m_p}{\mu_n}\frac{Z_a+Z_b}{2} + \frac{m_p}{\mu_n R^2}\frac{1}{\imath\hbar}\{(R_{\mathrm{CM},z} - R_{a,z}) + (R_{\mathrm{CM},z} - R_{b,z})\} \\
& \times \left\langle \Psi_0^{(0)} \middle| \sum_i [r_{i,y}, l_{i,x}(\vec{R}_{\mathrm{CM}})] \middle| \Psi_0^{(0)} \right\rangle - \frac{m_p}{2\mu_n R^2}\frac{1}{\imath\hbar} \\
& \times \{(R_{\mathrm{CM},z} - R_{a,z})^2 + (R_{\mathrm{CM},z} - R_{b,z})^2\} \left\langle \Psi_0^{(0)} \middle| \sum_i [r_{i,y}, p_{i,y}] \middle| \Psi_0^{(0)} \right\rangle
\end{aligned} \tag{1.37}$$

Evaluating the commutators

$$\langle \Psi_0^{(0)} \mid \sum_i [r_{i,\alpha}, p_{i,\beta}] \mid \Psi_0^{(0)} \rangle = \imath\hbar N \delta_{\alpha\beta} \tag{1.38}$$

$$\langle \Psi_0^{(0)} \mid \sum_i [r_{i,\alpha}, l_{i,\beta}(\vec{R}_{\mathrm{CM}})] \mid \Psi_0^{(0)} \rangle = \imath\hbar \epsilon_{\alpha\beta\gamma} \langle \Psi_0^{(0)} \mid \sum_i (r_{i,\gamma} - R_{\mathrm{CM},\gamma}) \mid \Psi_0^{(0)} \rangle \tag{1.39}$$

in which N is the total number of electrons, identifying the z-component of the electric dipolar moment in a system of coordinates fixed in the molecule, calculated with the origin of the coordinate system at the centre of mass, as

$$\begin{aligned} d_z(R;\vec{R}_{\mathrm{CM}}) &= e\{Z_a(R_{a,z} - R_{\mathrm{CM},z}) + Z_b(R_{b,z} - R_{\mathrm{CM},z})\} \\ &\quad - e\langle \Psi_0^{(0)} \mid \sum_i (r_{i,z} - R_{\mathrm{CM},z}) \mid \Psi_0^{(0)} \rangle \end{aligned} \tag{1.40}$$

and assuming a neutral molecule, for which $Q = Z_a + Z_b - N = 0$ and the dipolar moment is independent of the coordinate system, one obtains

$$g_r^{irr}(R) = g_r(R) - \frac{m_p}{e\mu_n} d_z(R) \frac{(R_{a,z} - R_{\mathrm{CM},z}) + (R_{b,z} - R_{\mathrm{CM},z})}{R^2} \tag{1.41}$$

Choosing arbitrarily the coordinate system in such a way that $R_{a,z} - R_{\mathrm{CM},z} = -R\ \mu_n/m_a$, which implies for a molecule of polarity $^+\mathrm{AB}^-$ that $d_z < 0$, one expresses the rotational g factor in terms of the electric dipolar moment and an irreducible nonadiabatic contribution g_r^{irr},

$$g_r(R) = g_r^{irr}(R) - \frac{m_p}{eR} d_z(R) \left(\frac{1}{m_a} - \frac{1}{m_b}\right) \tag{1.42}$$

According to the same arguments, g_r^a and g_r^b of a neutral molecule can be related to the electric dipolar moment [22,23],

$$g_r^a(R) = g_r(R) + \frac{2m_p}{eR} \frac{d_z(R)}{m_a} \tag{1.43}$$

$$g_r^b(R) = g_r(R) - \frac{2m_p}{eR} \frac{d_z(R)}{m_b} \tag{1.44}$$

The reverse relations for rotational g factor and electric dipolar moment expressed in terms of g_r^a and g_r^b are

$$g_r(R) = \mu_n \left(\frac{g_r^a(R)}{m_b} + \frac{g_r^b(R)}{m_a}\right) \tag{1.45}$$

$$d_z(R) = \frac{eR\mu_n}{2m_p} (g_r^a(R) - g_r^b(R)) \tag{1.46}$$

The latter four equations become important in the context of analysis of vibration–rotational spectra discussed in Section II.E.

Radial functions $g_r(R)$ and $g'_r(R)$ for the rotational g factor of a diatomic molecule in two isotopic variants are related to a radial function for electric dipolar moment [24–26]. For a fixed internuclear separation R, the rotational g factors g_r and g'_r of two variants differ because of disparate reduced masses in the moments of inertia I and I' and because of displacement of the center of mass $R'_{\text{CM}} - R_{\text{CM}}$. The expression for the rotational factor g'_r of a variant,

$$\begin{aligned} g'_r(R) &= \frac{m_p}{\mu'_n R}\left[Z_a(R_{a,z} - R'_{\text{CM}}) + Z_b(R_{b,z} - R'_{\text{CM}})\right] \\ &\quad + \frac{2m_p}{m_e \mu'_n R^2} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}'_{\text{CM}}) \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}'_{\text{CM}}) \mid \Psi_0^{(0)} \rangle}{E_0 - E_n} \end{aligned} \tag{1.47}$$

can then be rewritten in terms of the rotational factor g_r of a reference molecule and the electric dipolar moment following a derivation corresponding to Eqs. (1.35) through (1.42),

$$\mu'_n R g'_r(R) = \mu_n R g_r(R) - \frac{2m_p}{e} d_z(R; R_{\text{CM}})\left(R'_{\text{CM}} - R_{\text{CM}}\right) + m_p Q\left(R'_{\text{CM}} - R_{\text{CM}}\right)^2 \tag{1.48}$$

in which $Q = Z_a + Z_b - N$ denotes the total charge number of the molecule.

4. *Relation Between Rotational g Factor and Electric Quadrupolar Moment*

The rotational g factor and magnetizability are related to a tensor for molecular electric quadrupolar moment; its only finite component Q_{zz} for a diatomic molecule with its nuclei along the z-axis is given as

$$\begin{aligned} Q = Q_{zz} &= \frac{1}{2} e \sum_k Z_k (3R_{k,z}^2 - R_k^2) - \frac{1}{2} e \left\langle \Psi_0^{(0)} \middle| \sum_i (3r_{i,z}^2 - r_i^2) \middle| \Psi_0^{(0)} \right\rangle \\ &= e \sum_k Z_k R_{k,z}^2 - e \left\langle \Psi_0^{(0)} \middle| \sum_i \left(r_{i,z}^2 - \frac{1}{2}\{r_{i,x}^2 + r_{i,y}^2\} \right) \middle| \Psi_0^{(0)} \right\rangle \end{aligned} \tag{1.49}$$

Comparison of the first term with Eq. (1.27) and the second with Eq. (1.9) shows that Q_{zz} is expressible as

$$Q_{zz} = \frac{eI}{m_p}(g_r - g_r^e) - \frac{4m_e}{e}(\xi_\parallel^d - \xi_\perp^d) \tag{1.50}$$

Insertion of Eq. (1.26) gives

$$\begin{aligned} Q_{zz} &= \frac{eI}{m_p}\left(g_r + \frac{4m_p m_e}{e^2 I}\xi_\perp^p\right) - \frac{4m_e}{e}(\xi_\parallel^d - \xi_\perp^d) \\ &= \frac{eI}{m_p}g_r + \frac{4m_e}{e}\xi_\perp^p - \frac{4m_e}{e}(\xi_\parallel^d - \xi_\perp^d) \end{aligned} \tag{1.51}$$

Noting that $\xi_\parallel^p = 0$ for diatomic molecules, one obtains a relation between molecular electric quadrupolar moment, rotational g factor and anisotropy of magnetizability:

$$Q_{zz} = \frac{eI}{m_p}g_r - \frac{4m_e}{e}(\xi_\parallel - \xi_\perp) \tag{1.52}$$

D. Relation of Rotational *g* Factor to an Effective Hamiltonian

The time-independent Schrödinger equation for a diatomic molecule in an electronic state n of class ${}^1\Sigma^+$ or 0^+ is written as

$$H\left|\Theta_{n,vJM}(\vec{r},R)\right\rangle = E_{n,vJ}\left|\Theta_{n,vJM}(\vec{r},R)\right\rangle \tag{1.53}$$

in which J and M are conventional rotational quantum numbers and H is the molecular Hamiltonian [27–29] without spin and without translation of the molecule:

$$H = \frac{1}{2m_e}\sum_i \vec{p}_i^{\,2} + V - \frac{\hbar^2}{2\mu_n}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_n R^2}(\vec{J} - \vec{L})^2 + \frac{1}{2(m_a + m_b)}\left(\sum_i \vec{p}_i\right)^2 \tag{1.54}$$

The total angular momentum $\vec{J}$ is about the molecular center of mass; the electronic angular momentum $\vec{L} = \sum_i \vec{l}_i(R_{\mathrm{NCM}})$ is defined with respect to the centre of nuclear masses m_a and m_b; μ_n is the nuclear reduced mass defined in relation to Eq. (1.27), and V is the complete interparticle coulombic potential. The molecular wave function $\Theta_{n,vJM}(\vec{r},R)$ is a function of both electronic coordinates $\vec{r}$ and internuclear distance R. Approximate solutions to this equation are normally obtained by an approximate separation of nuclear and electronic coordinates. To do so one first solves the electronic Schrödinger equation,

$$\left(\frac{1}{2m_e}\sum_i \vec{p}_i^{\,2} + V\right)\left|\Psi_n^{(0)}(\vec{r};R)\right\rangle = V_{\mathrm{BO}}(R)\left|\Psi_n^{(0)}(\vec{r};R)\right\rangle \tag{1.55}$$

yielding a complete set of electronic wave functions $\{\Psi_n^{(0)}\}$ to be used in an *ansatz* for molecular wave functions,

$$\Theta_{n,vJM}(\vec{r}, R) = \sum_n \Psi_n^{(0)}(\vec{r}; R)\Phi_{vJM}^n(R) \tag{1.56}$$

With this *ansatz*, an effective Hamiltonian for rotational and vibrational motion of nuclei in an electronic state is obtained by projecting the Schrödinger equation [Eq. (1.53)] on electronic state $\langle\Psi_0^{(0)}(\vec{r}; R)|$. Before doing so, one transforms unitarily the molecular Hamiltonian [30],

$$\tilde{H} = e^{-\imath\lambda S} H e^{\imath\lambda S} = \tilde{H}^{(0)} + \lambda\tilde{H}^{(1)} + \lambda^2\tilde{H}^{(2)} + \cdots \tag{1.57}$$

in which the Hermitian operator S is determined so that the transformed Hamiltonian $\tilde{H}$ does not couple different electronic wave functions through first order, i.e.,

$$\langle\Psi_0^{(0)} \mid \tilde{H}^{(1)} \mid \Psi_n^{(0)}\rangle = 0 \tag{1.58}$$

In order zero, the Born–Oppenheimer approximation is recovered,

$$\left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu R^2}\vec{J}^2 + V_{\mathrm{BO}}(R)\right\}\Phi_{vJM}^n(R) = E_{vJ}\Phi_{vJM}^n(R) \tag{1.59}$$

With terms kept through second order the effective vibration–rotational Hamiltonian becomes [23,30–32]

$$\begin{aligned} H^{\mathit{eff}} = &-\frac{\hbar^2}{2\mu_n}\left(1 + \frac{2\hbar^2}{\mu_n}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)} \mid \frac{\partial}{\partial R} \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \frac{\partial}{\partial R} \mid \Psi_0^{(0)}\rangle}{E_0 - E_n}\right)\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_n R^2} \\ &\times\left(1 + \frac{2}{\mu_n R^2}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\sum_i l_{i,x}(\vec{R}_{\mathrm{NCM}})|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\sum_i l_{i,x}(\vec{R}_{\mathrm{NCM}})|\Psi_0^{(0)}\rangle}{E_0 - E_n}\right)\vec{J}^2 \\ &+ V_{\mathrm{BO}}(R) + V_{ad}(R) \end{aligned} \tag{1.60}$$

The term $V_{ad}(R)$ to describe adiabatic effects, according to which potential energy of the nuclei, of masses m_a and m_b, depends on not only internuclear separation R but also relative nuclear momenta [23,30–33], i.e.,

$$\begin{aligned} V_{ad}(R) = &-\frac{\hbar^2}{2\mu_n}\left\langle\Psi_0^{(0)}\left|\frac{\partial^2}{\partial R^2}\right|\Psi_0^{(0)}\right\rangle + \frac{1}{2\mu_n R^2}\langle\Psi_0^{(0)}|L_x^2 + L_y^2|\Psi_0^{(0)}\rangle \\ &+ \frac{1}{2(m_a + m_b)}\left\langle\Psi_0^{(0)}\left|\Big(\sum_i \vec{p}_i\Big)^2\right|\Psi_0^{(0)}\right\rangle, \end{aligned} \tag{1.61}$$

supplements the ordinary function $V_{\mathrm{BO}}(R)$ for the Born–Oppenheimer potential energy governing nuclear motions. Contributions to $V_{ad}(R)$ in this equation involve only expectation values of pertinent operators within the electronic state of interest, in the present case the electronic ground state.

The nonadiabatic terms, which involve matrix elements between the electronic state of interest, $\Psi_0^{(0)}$, and other, excited, electronic states, $\Psi_n^{(0)}$, are divided according to the symmetry of the molecule into one involving $\partial^2/\partial R^2$ and two orthogonal terms, exhibited in J^2 [23,30–33]:

$$H_{nad}^{eff} = -\frac{\hbar^4}{\mu_n^2}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)} \mid \frac{\partial}{\partial R} \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \frac{\partial}{\partial R} \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\frac{\partial^2}{\partial R^2} + \frac{1}{\mu_n^2 R^4}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{NCM}}) \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid \sum_i l_{i,x}(\vec{R}_{\mathrm{NCM}}) \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\vec{J}^2 \tag{1.62}$$

Comparison with Eq. (1.25) shows that the rotational inertial correction is related to the electronic contribution to the rotational g factor and the rotational term in the effective Hamiltonian becomes

$$H_r^{eff} = \frac{1}{2\mu_n R^2}\left(1 + \frac{m_e}{m_p}g_r^e(R)\right)\vec{J}^2 = \frac{1}{2\mu_n R^2}\left(1 + \frac{m_e}{m_p}g_r(R) - \frac{m_e}{m_p}g_r^n(R)\right)\vec{J}^2 \tag{1.63}$$

As the nuclear reduced mass μ_n is approximately related [32,33] to the atomic reduced mass μ,

$$\frac{1}{\mu_n} \approx \frac{1}{\mu}\left(1 - m_e\frac{Z_a m_b^2 + Z_b m_a^2}{m_a m_b(m_a + m_b)}\right) = \frac{1}{\mu}\left(1 - \frac{m_e}{m_p}g_r^n\right) \tag{1.64}$$

The rotational term in the effective Hamiltonian becomes

$$H_r^{eff} \approx \frac{1}{2\mu R^2}\left(1 + \frac{m_e}{m_p}g_r(R)\right)\vec{J}^2 \tag{1.65}$$

A similar derivation applies to the electronic contribution to the vibrational inertial correction [32,33], thereby defining a vibrational g factor, $g_v(R)$.

An effective equation of Schrödinger's type for nuclear motion is then [32]

$$\left\{-\frac{\hbar^2}{2\mu}\left(1+\frac{m_e}{m_p}g_v^e(R)\right)\frac{\partial^2}{\partial R^2}+\frac{1}{2\mu R^2}\left(1+\frac{m_e}{m_p}g_r(R)\right)\vec{J}^2 + V_{\mathrm{BO}}(R)+V_{ad}(R)\right\}\Phi^n_{vJM}(R)=E_{vJ}\Phi^n_{vJM}(R) \tag{1.66}$$

The point of interest in this article concerns $g_r(R)$, that is, a radial function postulated to express the dependence of the rotational g factor on internuclear distance according to separate treatment of electronic and nuclear motions. We discuss both experimental and theoretical means of determining this quantity. The vibrational g factor receives much less attention; we are aware of no calculation of it with the full sum-over-states expression in Eq. (1.62).

II. EXPERIMENTAL METHODS

The various experimental methods of determining the quantity $g_r(R)$ include spectral methods, with measurement of a frequency or intensity that varies with strength of external magnetic field, or use of molecular beams in magnetic fields with or without spectral transitions, and even spectral methods with no applied field. These methods yield information of distinct kinds about the rotational g factor. From molecular beams with spectral transitions (Section II.A), and from application of the Zeeman effect on microwave spectra (Section II.B), one obtains an expectation value of the rotational g factor for a particular vibration–rotational state. For a molecular beam without spectral transition (Section II.A), the observable quantity is only a statistical average over vibration–rotational states populated at the temperature of the experiment. From analysis of magnetic circular dichroism of rotationally resolved vibrational transitions (Section II.D), one obtains a poorly defined average of expectation values. Frequency data from spectra of samples without fields (Section II.E) yield a rough value of the radial function for rotational g factor at the equilibrium bond length.

A. Molecular Beams

When molecules lacking net electronic orbital and spin angular momentum in a beam pass a region in which they are subjected to an inhomogeneous magnetic field, deflection of the beam occurs because of an intrinsic nuclear magnetic moment, a magnetic moment that may be induced diamagnetically in the molecules by the applied field, or a rotational magnetic moment that the molecule acquires by virtue of its rotational angular momentum [15]. All these moments are of order a nuclear magneton (5×10^{-27} A m^{-2} or J T^{-1}) or less. This technique was first applied to measure the rotational magnetic moment of $^{1}H_2{}^{16}O$ [34]. Measurements on $^{1}H_2$, $^{1}H^{2}H$, and $^{2}H_2$ in the same laboratory [8,9] yielded values of magnetic moments of the proton and deuteron and of the rotational magnetic moment; for *para*-$^{1}H_2$ for which the resultant angular momentum due to nuclear spin is $I = 0$, deflection is due entirely to rotational angular momentum, whereas in the case of *ortho*-$^{1}H_2$ deflection is due to the combined moments from nuclear spin and molecular rotation. Values of g_r for $^{1}H_2$ obtained in these early experiments are mentioned above.

Precision of such measurements is greatly enhanced on introduction of another electric or magnetic field oscillating at frequency ν; if this frequency matches the differences between energies of two orientation states of the molecule divided by Planck's constant, a resonance condition exists such that energy is transferred from the field to the molecule. Under these conditions the perceived intensity of the beam, otherwise directed with adjacent fields to reach the detector, decreases, indicating occurrence of a spectral transition; hence the sensitivity and precision of the experiment are greatly enhanced. By this means, with magnetic resonance for $^{1}H_2$ in the ground vibrational state $v = 0$ and rotational state $J = 1$ (expressed as $|0, 1\rangle$), the rotational magnetic moment $g_r = 0.88291 \pm 0.00007$ [35] was measured, distinct from $g_r = 0.882265 \pm 0.000035$ for $|0, 2\rangle$ [36]. The quantity measured in this experiment is an expectation value of a radial function $g_r(R)$ in a particular vibration–rotational state, i.e., $\langle vJ|g_r(R)|vJ\rangle$ according to Eq. (5.3); without an additional magnetic field and spectral transition in an experiment to distinguish a specific vibration–rotational state, the quantity obtained is some average of expectation values over states populated at the effective temperature of the experiment. The sign of g_r might be determined by comparison with that of a known nuclear spin using rotating magnetic fields [37] or from the asymmetry introduced by second-order effects [11], but in some cases, such as $^{15}N_2$ [38], the sign is not yet determined.

For electrically nonpolar molecular species, a molecular beam with magnetic resonance generally serves to determine g_r; for compounds with a finite molecular electric dipolar moment, either a molecular beam with electric resonance or the Zeeman effect on pure rotational transitions in the microwave region is typically employed. With multiple fields acting on a beam causing many successive transitions, each $|\Delta M_J| = 1$, the net alteration of magnetic dipolar moment is large; by this means small magnitudes of g_r might still be measured [37,39]. When results from molecular beams and magnetic resonance (MB–MR) with multiple quanta are compared with those from electric resonance (MB–ER), however, large disparities occur, when molecules have large nuclear quadrupolar interaction. For instance, values for $^7Li^{35}Cl$ $g_r = 0.0848 \pm 0.0032$ [40] (MB–MR) and 0.100419 ± 0.000031 [41] (MB–ER) and for $^7Li^{79}Br$ $g_r = 0.0911 \pm 0.0039$ [40] (MB–MR) and 0.112056 ± 0.000064 [42] (MB–ER) are reported from these respective techniques, practised in the same laboratory. Because there are many excited rotational states and strong coupling between a nuclear spin and rotational angular momentum, the method employing magnetic resonance and multiple quanta was deemed unreliable, and the corresponding results were repudiated [42]. In the compilation in the Appendix to this article, these corresponding results are included with a question mark in parentheses to indicate their questionable accuracy; in some cases subsequent values have not superseded them.

B. Microwave Spectrometry With Zeeman Effect

As mention in the Introduction to this article, application of an external magnetic field to a gaseous sample contained in a conventional waveguide can produce a splitting of spectral lines measured in the microwave spectral region 10–100 GHz [1–4]. For a rotational state labeled with quantum number J for total angular momentum, there exist $2J + 1$ values of magnetic quantum number M_J. According to Eq. (1.31), an effective rotational Zeeman Hamiltonian [43] for interaction between a rotating molecule and an external magnetic field of flux density $\vec{B}$ is, including only the term linear in $\vec{B}$,

$$H = -\frac{\mu_N}{\hbar}\vec{B}\mathbf{g}_r\vec{J} \tag{2.1}$$

The energy of interaction ΔE for a diatomic molecule is therefore

$$\Delta E_{JM_J} = -\frac{\mu_N}{\hbar}\langle v, J, M_J|\vec{B}\mathbf{g}_r\vec{J}|v, J, M_J\rangle = -\mu_N\langle v, J|g_r|v, J\rangle M_J B \tag{2.2}$$

When the electric vector of radiation is parallel to the direction of the magnetic field (π components), the selection rules are $\Delta J = J' - J = +1$ and $\Delta M_J = 0$; the single observed line with frequency ν_0, when the magnetic field is lacking, is split into $2J + 1$ components,

$$\nu = \nu_0 + [\langle v, J|g_r|v, J\rangle - \langle v, J'|g_r|v, J'\rangle]M_J\frac{\mu_N}{h}B \tag{2.3}$$

When the electric vector of radiation is perpendicular to the applied magnetic field (σ components), the selection rules are $\Delta J = J' - J = +1$ and $\Delta M_J = \pm 1$; and a pattern of $2(2J + 1)$ Zeeman components