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$$\nu = \nu_0 + ([\langle v, J|g_r|v, J\rangle - \langle v, J'|g_r|v, J'\rangle]M_J \pm \langle v, J'|g_r|v, J'\rangle)\frac{\mu_N}{h}B \quad (2.4)$$

When $\langle v, J|g_r|v, J\rangle$ varies little with J, π components show no Zeeman effect and σ components are all superimposed into two lines with frequencies

$$\nu = \nu_0 \pm \langle v, J'|g_r|v, J'\rangle \frac{\mu_N}{h}B \quad (2.5)$$

or

$$(\nu - \nu_0)/10^6\,\mathrm{Hz} \approx \pm 7.6\langle v, J'|g_r|v, J'\rangle B/\mathrm{T} \quad (2.6)$$

By this means a magnitude of g_r is readily obtained, provided the displacement of these components much exceeds the width of spectral lines. To determine a sign of g_r requires use of circularly polarized microwave radiation; when a magnetic field is parallel to the direction of propagation of a circularly polarized microwave, only one component is excited, having all the intensity of the unsplit line [19]. The enhanced experimental complication of the latter method results in it seldom being applied; in many cases a sign of g_r is tacitly assumed. If a molecule contains nuclei having a quantum number for nuclear spin $|I| > \frac{1}{2}$ and thus having electric quadrupolar moments, at small densities of magnetic flux mixing occurs between substates of M_I and M_J; in this case a sign of g_r might be deduced if the nuclear g value is known [1]. In other cases in which molecular magnetizability is measured from quadratic dependence of energy on density of magnetic flux [see Eq. (1.31)], the molecular electric quadrupolar moment Q derived from g_r and the anisotropy of magnetizability [Eq. (1.52)], can serve as a criterion to select the sign of g_r: if Q has an expected magnitude with one possible sign of g_r, but not the other, the former sign is accepted.

For a transition from a state with rotational quantum number J to a state with $J + 1$, neglecting the dependence on J of $\langle v, J'|g_r|v, J'\rangle$, the quantity measured in these experiments is essentially g_r of the latter state, but is rigorously so in the common case of the transition from a state with $J = 0$ to another with $J = 1$ [1] because a molecule with $J = 0$ has no rotational angular momentum. Thus, for this experiment a measurement produces a value of $g_r = \langle v, J+1|g_r|v, J+1\rangle$, or more generally a magnitude of this quantity.

After 1955, for several decades this spectral method was the one most commonly applied to yield accurate magnitudes of rotational g factors, even though the Zeeman effect was invoked less widely than the Stark effect. One reason for this application is that sensitivity of detection in the microwave spectral region relative to a dc signal is much enhanced by means of Stark modulation of rotational absorption lines [44], generally about 100 kHz with the concomitant minimum width of spectral line. A displacement of a spectral line when an electric field is applied is proportional to the squared strength of the field, and the factor of proportionality involves the square of the electric dipolar moment (or its expectation value) [1]; as the electric field between parallel plates in a wave guide is readily altered on varying the electric potential between them, almost any conventional microwave spectrometer operated during that period yielded magnitudes of electric dipolar moments practically as readily as frequencies of rotational transitions. In the millimeter-wave region, modulation of the source frequency is generally preferable because much power at those frequencies is lost in conventional cells designed to accommodate measurement of the Stark effect; for this reason, measurements of electric dipolar moments in this region are few unless recourse is made to a short cell of waveguide type [45]. When the Zeeman effect was applied to the same molecular species in an electronic state of class $^1\Sigma^+$ or 0^+, the primary objective was measurement of the rotational g factor whether or not that information for isotopic species was combined with knowledge of the magnitude of the electric dipolar moment to yield the sense of that moment. As microwave spectrometers constructed since 1985 have tended to be used with gaseous jets in a large and almost spherical cavity [46], both Stark and Zeeman effects are applicable only with difficulty because dimensions of resonators forming the cavity are so large that accessible electric potential differences applied between Stark electrodes distant from one another yield only small electric fields, although the small widths of spectral lines provide greatly enhanced sensitivity; with spectrometers of traditional form consisting of samples enclosed in waveguides, one can still use the desired Fourier-transform method [47], but the sensitivity is greatly inferior to that obtained with samples prepared in pulsed jets. The rates of newly reported values of both electric moments and rotational g factors have hence decreased, and other methods to measure these quantities have been devised partly to compensate for this deficiency in the case of microwave spectrometry.

C. Magnetic Resonance in the Far Infrared Region

In a conventional experiment employing magnetic resonance in the far infrared region [48], a laser at a fixed frequency dependent on the difference between energies of particular eigenstates of a molecular emitter such as vapors of H_2O or CH_3OH subjected to electric discharge provides a beam of monochromatic radiation in the far infrared spectral region, $\tilde{\nu} < 5 \times 10^5\ \mathrm{m}^{-1}$. That light passes through a gaseous sample contained in a suitable vessel located between poles of a magnet that provides a homogeneous magnetic field variable continuously within a given range. In general, no frequency of a pure rotational transition of molecules in the gaseous sample coincides with a frequency emitted from the laser source. On application of a variable magnetic field, energies of molecules are altered such that the frequency of a transition can approach a resonance condition with that of the source. If possible frequencies of molecules in the sample are known accurately in the absence of magnetic field, measurement of that field at the condition of resonance indicates the magnitude of g_r according to Eq. (2.5). No such measurement of rotational g factor is yet reported for a molecular species in an electronic state of class ${}^1\Sigma^+$ or 0^+, but analyses of spectra of free radicals in other electronic states have produced their values of g_r; for instance, for OH^+ in electronic state $a^1\Delta$ with $v = 0$, $g_r = -0.001815 \pm 0.000018$ [49].

This technique is expected to be applicable particularly to a diatomic molecular species having a small moment of inertia, for which pure rotational transitions lie beyond the microwave spectral region in which a conventional procedure for the Zeeman effect is readily implemented. Compared with application of magnetic resonance on transitions of molecules with net electronic angular momentum, this method applied to molecules in electronic state ${}^1\Sigma^+$ or 0^+ would generally require a larger range of tuning of a magnetic field to achieve a condition of resonance, thus effectively requiring a larger maximum field for this experiment. Combination of this required condition of magnetic resonance with use of a molecular beam in order to diminish the width of spectral lines due to distribution of a parallel component of molecular velocities is expected to enhance the sensitivity and precision of this approach, but the range of transitions might then be limited to those involving small values of J; information on a slight variation of g_r with J might still be obtained.

D. Infrared Spectrometry and Magnetic Circular Dichroism

Circular dichroism, which signifies differential absorption of circularly polarized radiation, is induced in all matter that is subjected to a uniform longitudinal magnetic field. The ratio of this difference $\Delta A = A_- - A_+$ of absorbance between left and right circularly polarized light, called magnetic circular dichroism, to the total absorbance $A = \frac{1}{2}(A_+ + A_-)$ in the absence of a magnetic field is linearly proportional to the density of magnetic flux. In application to a vibration-rotational spectrum of a diatomic molecule [50,51] in an electronic state of class ${}^1\Sigma^+$ or 0^+, a transition from a state $|0, 1\rangle$ to another state with $|v', 0\rangle$, i.e., the first line in a P branch of a particular band, we consider for purposes of explanation. On application of a longitudinal magnetic field, substates of various M_J for $J = 1$ lose their degeneracy, such that a transition from a substate $J = 1$, $M_J = 1$ to a state $J' = 0$, $M_J = 0$ occurs with right circularly polarized light at a frequency greater than that of the undisplaced line (in the absence of magnetic field), whereas a transition from $J = 1$, $M_J = -1$ occurs at a smaller frequency; the two lines from the Zeeman effect have opposite phases. With B_0 about 10 T and optical resolution 50 m^{-1} near 2×10^5 m^{-1}, the order of magnitude of a ratio $\Delta A/A$ is 10^{-4}; under these conditions, splitting between two lines is much less than the resolution, and also possibly less than the width of the line due to the distribution of molecular velocities in a static sample. With moment analysis [52] of rotationally resolved bands, the sign and magnitude of the rotational g factor can nevertheless be determined. The parameter A_1/D_0 [50,53,54],

$$\frac{A_1}{D_0} = \frac{1}{B\mu_B} \frac{\langle \Delta A \rangle_1}{\langle A \rangle_0} \tag{2.7}$$

is thus obtained from the zeroth moment of absorbance $\langle A \rangle_0$ and the first moment $\langle \Delta A \rangle_1$, defined as [52]

$$\langle A \rangle_0 = \int \frac{A}{\nu} d\nu \tag{2.8}$$

$$\langle \Delta A \rangle_1 = \int \frac{\Delta A}{\nu} (\nu - \nu_0) d\nu \tag{2.9}$$

for which the frequency ν_0 is chosen to be

$$\nu_0 = \frac{\int A d\nu}{\int \frac{A}{\nu} d\nu} \tag{2.10}$$

which implies that the first moment of the absorbance $\langle A \rangle_1$ is zero. For a dilute gaseous sample consisting of molecules in an electronic state of class ${}^1\Sigma^+$, an external flux density B interacts with a rotationally induced magnetic dipolar moment of a molecule according to the effective rotational Zeeman Hamiltonian in Eq. (2.1). Generalization [50,54] of the rigid shift expression for electronic magnetic circular dichroism [52] to the vibration–rotational case gives the following expressions for parameters A_1 and D_0:

$$\begin{aligned} A_1 = &-\frac{1}{d_J} \frac{\mu_N}{\mu_B} \sum_{M_J, M_{J'}} (|\langle v, J, M_J \mid d_- \mid v', J', M_{J'} \rangle|^2 - |\langle v, J, M_J \mid d_+ \mid v', J', M_{J'} \rangle|^2) \\ &\times (\langle v', J' \mid g_r \mid v', J' \rangle \langle v', J', M_{J'} \mid J_z \mid v', J', M_{J'} \rangle \\ &- \langle v, J \mid g_r \mid v, J \rangle \langle v, J, M_J \mid J_z \mid v, J, M_J \rangle) \end{aligned} \tag{2.11}$$

$$D_0 = \frac{1}{2d_J} \sum_{M_J, M_{J'}} (|\langle v, J, M_J \mid d_- \mid v', J', M_{J'} \rangle|^2 + |\langle v, J, M_J \mid d_+ \mid v', J', M_{J'} \rangle|^2) \tag{2.12}$$

in which $d_{\pm} = 1/\sqrt{2}(d_+ \pm d_-)$ is the operator for electronic dipolar moment for right (+) and left (−) circularly polarized light and d_J is the degeneracy of state $| v, J, M_J\rangle$. Application of the selection rule $\Delta M = \pm 1$ for left and right circularly polarized light yields a simple expression for the ratio A_1/D_0 for the transition $R(0)$ from $J = 0$ to $J' = 1$,

$$\frac{A_1}{D_0} = -2\frac{\mu_N}{\mu_B}\langle v', 1 \mid g_r \mid v', 1\rangle \tag{2.13}$$

and for the transition $P(1)$ from $J = 1$ to $J' = 0$,

$$\frac{A_1}{D_0} = -2\frac{\mu_N}{\mu_B}\langle v, 1 \mid g_r \mid v, 1\rangle \tag{2.14}$$

whereas, for example, for the transition $R(1)$ from $J = 1$ to $J' = 2$, A_1 and D_0 are obtained as

$$\begin{aligned} A_1 = -\frac{1}{d_1}\frac{\mu_N}{\mu_B}\{&|\langle v,1,1 \mid d_- \mid v',2,2\rangle|^2(2\langle v,2 \mid g_r \mid v,2\rangle - \langle v',1 \mid g_r \mid v',1\rangle) \\ &+ |\langle v,1,1 \mid d_+ \mid v',2,0\rangle|^2\langle v',1 \mid g_r \mid v',1\rangle \\ &+ |\langle v,1,0 \mid d_- \mid v',2,1\rangle|^2\langle v,2 \mid g_r \mid v,2\rangle \\ &+ |\langle v,1,0 \mid d_+ \mid v',2,-1\rangle|^2\langle v,2 \mid g_r \mid v,2\rangle \\ &+ |\langle v,1,-1 \mid d_- \mid v',2,0\rangle|^2\langle v',1 \mid g_r \mid v',1\rangle \\ &+ |\langle v,1,-1 \mid d_+ \mid v',2,-2\rangle|^2(2\langle v,2 \mid g_r \mid v,2\rangle - \langle v',1 \mid g_r \mid v',1\rangle)\} \end{aligned} \tag{2.15}$$

$$\begin{aligned} D_0 = \frac{1}{2d_1}\{&|\langle v,1,1 \mid d_- \mid v',2,2\rangle|^2 + |\langle v,1,1 \mid d_+ \mid v',2,0\rangle|^2. \\ &+ |\langle v,1,0 \mid d_- \mid v',2,1\rangle|^2 + |\langle v,1,0 \mid d_+ \mid v',2,-1\rangle|^2 \\ &+ |\langle v,1,-1 \mid d_- \mid v',2,0\rangle|^2 + |\langle v,1,-1 \mid d_+ \mid v',2,-2|^2\} \end{aligned} \tag{2.16}$$

The rotational g factor in rotational state $J = 1$ of the lower v and upper v' vibrational states can therefore be obtained from transitions $R(0)$ and $P(1)$, respectively. The ratio A_1/D_0 of the transition $R(1)$ allows no extraction of the rotational g factor without an approximation that rotational g factors in lower and upper vibrational states are the same and that they are independent of rotational quantum number. In practice, because experiments on magnetic vibrational circular dichroism have large error resulting from measurement of intensity rather than frequency, ratios A_1/D_0 of all lines in a branch are commonly averaged and a rotational g factor $\langle g_r \rangle$ averaged in some way is obtained:

$$\langle g_r \rangle = -2 \frac{\mu_B}{\mu_N} \frac{A_1}{D_0} \tag{2.17}$$

The accuracy of g_r is moderate at best; for instance, for $^{12}C^{16}O$ in a transition $v = 1 \leftarrow v = 0$, measurements of 14 lines in the P branch and 25 lines in the R branch yielded a value $g_r = -0.262 \pm 0.026$ [50], compared with a value $g_r = -0.26890 \pm 0.00010$ from a sample in a molecular beam with magnetic resonance for detection [55], hence a frequency measurement. The sign of g_r is nevertheless readily determined. Improved optical resolution is expected to enhance the sensitivity and precision of these experiments.

E. Frequency Data From Samples Without Applied Fields

Whereas eigenvalues of vibration–rotational energy $\tilde{E}_{vJ}$, or spectral terms, in Eq. (1.59) (or equivalent), are expressed in a form [56]

$$\tilde{E}_{vJ} = \sum_{k=0} \sum_{l=0} Y_{kl} \left(v + \frac{1}{2} \right)^k [J(J+1)]^l, \tag{2.18}$$

the corresponding eigenvalues $\tilde{E}_{vJ}$ in Eq. (1.66) have the form [57]

$$\tilde{E}_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b}) \left(v + \frac{1}{2} \right)^k [J(J+1)]^l \tag{2.19}$$

Hence, the primary term coefficients Y_{kl} pertain to mechanical effects, i.e., rotational and vibrational motions of nuclei about the center of molecular mass, whereas auxiliary term coefficients Z_{kl} of several kinds represent extramechanical effects, i.e., ones resulting from the fact that electrons fail to follow perfectly the mechanical motions of nuclei. Coefficients Z_{kl}^v for atomic center A or B incorporate additional vibration–rotational effects that depend on the mass of each separate atomic center rather than on atomic reduced mass μ, as do Y_{kl}; coefficients Z_{kl}^r take into account further rotational effects, also for each atomic center. To represent these effects, in radial functions we employ a reduced variable z [58,59] for displacement from equilibrium internuclear separation R_e

$$z \equiv 2 \frac{R - R_e}{R + R_e} \tag{2.20}$$

in which a factor 2 appears for convenience elsewhere. As this variable is well behaved at both limits of molecular existence, a united atom at $R = 0$ or $z = -2$ and separate atoms as $R \to \infty$ or $z \to 2$, boundary conditions are applicable [60]. With such an argument, we postulate radial functions as follows. For the part of internuclear potential energy independent of nuclear mass [57], we have

$$U_{\mathrm{BO}}(R) \to V(z) = c_0 z^2 \left(1 + \sum_{j=1} c_j z^j\right) \tag{2.21}$$

For other required radial functions that depend on the inverse mass of each separate nucleus A and B (in a diatomic molecule with $Z_a \neq Z_b$), we have for adiabatic effects [57]

$$U_{ad}(R) \to V'(z) = m_e \left(\frac{1}{M_a} \sum_{j=1} u_j^a z^j + \frac{1}{M_b} \sum_{j=1} u_j^b z^j\right) \tag{2.22}$$

for nonadiabatic rotational effects [57],

$$\frac{m_e}{m_p} g_r(R) \to \frac{m_e}{m_p} g_r(z) = m_e \left(\frac{1}{M_a} \sum_{j=0} t_j^a z^j + \frac{1}{M_b} \sum_{j=0} t_j^b z^j\right), \tag{2.23}$$

and for nonadiabatic vibrational effects [57],

$$\frac{m_e}{m_p} g_v(R) \to \frac{m_e}{m_p} g_v(z) = m_e \left(\frac{1}{M_a} \sum_{j=0} s_j^a z^j + \frac{1}{M_b} \sum_{j=0} s_j^b z^j\right) \tag{2.24}$$

Coefficients c_j, $u_j^{a,b}$, $t_j^{a,b}$, and $s_j^{a,b}$ serve as fitting parameters [57] in reduction of pure rotational and vibration–rotational spectra of a particular diatomic molecular species in multiple isotopic variants, measured in the absence of externally applied electric or magnetic field.

Comparison of Eqs. (2.23) and (1.45) shows that

$$g_r^a(z) = \frac{m_p}{\mu} \sum_{j=0} t_j^b z^j \tag{2.25}$$

$$g_r^b(z) = \frac{m_p}{\mu} \sum_{j=0} t_j^a z^j \tag{2.26}$$

and thus

$$t_0^a = \frac{\mu}{m_p} g_r^b(R_e) \tag{2.27}$$

$$t_0^b = \frac{\mu}{m_p} g_r^a(R_e) \tag{2.28}$$

Using these relations in Eqs. (1.35), (1.45), and (1.46) we obtain the following useful relations applicable to neutral molecules [22,32]:

$$g_r(R_e) = m_p\left(\frac{t_0^a}{M_a} + \frac{t_0^b}{M_b}\right) \tag{2.29}$$

$$g_r^{irr}(R_e) = \frac{m_p}{2\mu}(t_0^a + t_0^b) \tag{2.30}$$

$$d_z(R_e) = \frac{eR_e}{2}(t_0^b - t_0^a) \tag{2.31}$$

From the second coefficients t_1^a and t_1^b, in the expansion of the nonadiabatic rotational effects, Eq. (2.23), information about the derivatives of these properties can be obtained:

$$\left(\frac{\partial g_r(z)}{\partial z}\right)_{R_e} = m_p\left(\frac{t_1^a}{M_a} + \frac{t_1^b}{M_b}\right) \tag{2.32}$$

$$\left(\frac{\partial g_r^{irr}(z)}{\partial z}\right)_{R_e} = \frac{m_p}{2\mu}(t_1^a + t_1^b) \tag{2.33}$$

$$\left(\frac{\partial d_z(z)}{\partial z}\right)_{R_e} = \frac{eR_e}{2}(t_1^b - t_1^a) \tag{2.34}$$

Analogous results connect properties of functions $g_v^{irr}(z)$ and $g_v(z)$ at R_e to fitting parameters $s_j^{a,b}$ [57]. Functions $g_r^{irr}(z)$ and $g_v^{irr}(z)$ represent irreducible nonadiabatic effects, attributed to interactions between an electronic ground state of interest and electronically excited states, of classes $^1\Pi$ or 1 for g_r^{irr} and $^1\Sigma^+$ or 0^+ for g_v^{irr} [61], as shown in Eq. (1.35). The quantities $d_z(R_e)$ and $g_r(R_e)$ become the most meaningful values of the z-component of the permanent electric dipolar moment and of the rotational g factor at the equilibrium bond length, respectively. By means of these relations one can derive information about not only the rotational g factor at the equilibrium bond length but also of the electric dipolar moment of a molecule from spectral data—specifically, measurements of only transition frequencies of multiple isotopic variants—of gaseous samples without applied electric or magnetic field. This method has an additional advantage that it directly yields the signs (relative to a defined internuclear axis) of both $g_r(R_e)$ and $d_z(R_e)$. The principal disadvantage of this method is that for an atom of each type A or B there exist three radial functions, involving u_j, t_j, and s_j of that type, to be evaluated essentially from term coefficients of only two types, Z^r_{kl} and Z^v_{kl}; the precision of deduced parameters, reflecting uncertainty propagated ultimately from frequency data, is at present poorer than that resulting directly from application of Stark and Zeeman effects. An empirical observation that adiabatic effects seem much smaller than nonadiabatic effects for atomic centers with atomic numbers Z greater than about 10 [62] might enable a practical resolution of this indeterminacy, even though no theoretical justification of this observation is available [32]. With increasing atomic number, the effects of finite nuclear volume [63,64] might interfere with this approach unless they are taken into account separately.

III. THEORETICAL METHODS

A. General Considerations

Electronic structure calculations of rotational g factors have much in common with calculations of many other electric and magnetic properties of so-called second order such as NMR chemical shieldings [65], spin-rotational parameters [65], and electric dipolar polarizabilities [66]. All these properties are determined with relations similar to the one for $\boldsymbol{g}^e_r$ in Eq. (1.25).

They may be considered to be second-order terms, expressed in a classical way as a sum over unperturbed states, like the electronic contribution to the g factor in Eq. (1.25). A direct way to evaluate this expression would be to use a sum-over-states method according to which one somehow generates, to a good approximation, excited states in a complete set for the unperturbed system. This method has been applied to molecules having only two electrons [67,68]. For all but the simplest molecules, this approach is unfeasible; one must hence resort to other methods. The latter methods are classified in broad terms as either second-derivative methods or response methods. In the former, one exploits the fact that the electronic part of the g factor [see Eq. (1.31)] is the second derivative of total electronic energy with respect to rotational angular momentum and to density of magnetic flux:

$$g^e_{r,\alpha\beta} = -\frac{\hbar}{\mu_N}\frac{\partial^2 E(\vec{B},\vec{J})}{\partial B_\alpha \partial J_\beta} \tag{3.1}$$

Although this approach is impractical for magnetic properties, derivatives of this type in principle may be determined with numerical (i.e., finite-field) methods; such methods are used mainly to calculate electric polarizabilities. Techniques involving analytic derivatives have been formulated instead, as described in Section III.C.

The discussion in this section centers on how methods of the other, or second-derivative, class can be applied to calculate g_r^e and related molecular properties. These methods one refers to as polarization–propagator [69] or response [70] methods; their characteristic feature is that one computes the linear response of a system, i.e., a molecule, to an external perturbation. If the perturbation is an interaction of electronic and rotational motions, the one-electron property that we monitor becomes the magnetic dipolar moment; the linear response of the system is then the rotational g tensor. Hence in polarization–propagator theory one obtains the g tensor as a first-derivative, or linear response, of a property that is formally a first derivative of total energy; the one-electron property in question is magnetic dipolar moment. In an exact limit, this approach is thus equivalent to taking directly the second derivative of energy, i.e., it is identical to techniques involving analytic second derivatives discussed above. However, in approximate calculations, this equivalence might not hold, as the first derivative of total energy with respect to B is equal to magnetic dipolar moment only if the Hellmann–Feynman theorem [71,72] holds for the method in question. Variational methods such as the self-consistent field (SCF) method and its multiconfigurational extension, the multiconfigurational SCF (MCSCF) method, fulfill this criterion, unlike perturbative methods. Thus, numerical results, e.g., for rotational g tensors, using identical levels of electronic structure theory might vary depending on whether the properties are evaluated as linear response functions or as second derivatives of electronic energy. For instance, methods in both formulations based on second-order perturbation theory are called MP2 methods [73] in derivative techniques or SOPPA methods in propagator theory. These methods fail to yield the same numerical results; in some cases the second-order properties are quite disparate [74,75]. We proceed to describe these two approaches in detail.

B. Calculations of Polarization Propagators

A polarization propagator may formally be defined in either a time or an energy representation, which one can readily show to be the same [76]. In the temporal domain the propagator describes how a density disturbance develops or propagates from time t to time t'; this interpretation led to the name polarization propagator [77]. To relate the propagator more directly to second-order properties such as the rotational g tensor, it is instructive to define it directly in energy space using a language of response theory.

We consider the response of an average value of some one-electron operator A in a state $|0\rangle$, commonly called a reference state, to an external perturbation described with an operator B, C, etc. At time t the average value is

$$\langle A\rangle_t = \langle \Psi_0^{(0)} \mid A \mid \Psi_0^{(0)}\rangle + \int_{-\infty}^{\infty} \langle\langle A; B\rangle\rangle_{\omega+i\epsilon} e^{-i(\omega+i\epsilon)t} d\omega + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \langle\langle A; B, C\rangle\rangle_{\omega_1+i\epsilon_1,\omega_2+i\epsilon_2} e^{-i(\omega_1+i\epsilon_1+\omega_2+i\epsilon_2)t} d\omega_1 d\omega_2 + \cdots \tag{3.2}$$

In this equation, one defines response functions that are linear, e.g., $\langle\langle A; B\rangle\rangle_{\omega+i\epsilon}$, or quadratic, e.g., $\langle\langle A; B, C\rangle\rangle_{\omega_1+i\epsilon_1,\omega_2+i\epsilon_2}$, etc. Here ϵ_i are positive infinitesimals that ensure the effect of a perturbation to be zero at $t = -\infty$. Expressed in terms of unperturbed states, the real part of the linear response function has a form [70]

$$\langle\langle A; B\rangle\rangle_\omega = \sum_n \left\{ \frac{\langle \Psi_0^{(0)} \mid A \mid \Psi_n^{(0)}\rangle\langle \Psi_n^{(0)} \mid B \mid \Psi_0^{(0)}\rangle}{\hbar\omega - (E_0 - E_n)} - \frac{\langle \Psi_0^{(0)} \mid B \mid \Psi_n^{(0)}\rangle\langle \Psi_n^{(0)} \mid A \mid \Psi_0^{(0)}\rangle}{\hbar\omega + (E_0 - E_n)} \right\} \tag{3.3}$$

Comparison of this spectral representation with those of a tensor g_r^e in Eq. (1.25) based on a sum over states shows its relationship to the linear response function at $\omega = 0$ for $A = B = \sum_i \vec{l}_i(\vec{R}_{\mathrm{CM}})$. Calculations of a g tensor based on a polarization propagator thus involve finding a way to evaluate the response function without knowing all states in Eq. (3.3); the latter procedure implies a calculation of a sum over states that we seek to avoid.

The method of calculation that is applied involves finding another equation that determines the polarization propagator. Although the algebra underlying this derivation is beyond the scope of this article, the principles involved may be summarized. Using a temporally dependent equation of Heisenberg's type for operators that enter a definition of a temporally dependent polarization propagator [76], or, alternatively, corresponding fundamental equations in other representations [70,78], one can derive an equation different from Eq. (3.3) so as to determine the polarization propagator. The basic structure of this equation is

$$\langle\langle A;B\rangle\rangle_{\omega}^{SOPPA} = t^{(0,2)}(A,\omega)P^{(0,1,2)}(\omega)^{-1}\tilde{t}^{(0,2)}(B,\omega) + s^{(1)}(A)Q^{(0)}(\omega)^{-1}\tilde{s}^{(1)}(B) \tag{3.4}$$

This equation shows that matrices $t^{(0,2)}(A,\omega)$, $t^{(0,2)}(B,\omega)$, $s^{(1)}(A)$, and $s^{(1)}(B)$ for the transition moment all depend on a property that we seek to compute, unlike the so-called principal propagator, $P(\omega)$ [79]. The superscripts indicate order of perturbation theory, for which the perturbation is a fluctuation potential, i.e., the electronic Hamiltonian minus the sum of Fock operators for the molecule in its ground state. The polarization propagator in Eq. (3.4) represents the second-order polarization propagator approximation (SOPPA) to $\langle\langle A;B\rangle\rangle_{\omega}$ [80], signifying an approximation in perturbation theory correct through second order. The first-order polarization propagator approximation, normally called a random-phase approximation (RPA) or coupled Hartree–Fock (CHF) method, is the self-consistent field approximation to $\langle\langle A;B\rangle\rangle_{\omega}$ in which

$$\langle\langle A;B\rangle\rangle_{\omega}^{RPA} = \tilde{t}^{(0)}(A,\omega)P^{(0,1)}(\omega)^{-1}\tilde{t}^{(0)}(B,\omega) \tag{3.5}$$

To obtain a SOPPA method consistent through second order in the fluctuation potential, a correction to first order in the wave function for the reference state is needed, in order to evaluate both matrices t and P and the second-order correction from single substitutions for matrix $t^{(2)}$ [80]. Hence both first-order Rayleigh–Schrödinger coefficients and part of the second-order coefficients that originate from single substitution appear in SOPPA matrices [78]. We found [81,82] that, in many cases, results for computed properties are improved when the corresponding coupled-cluster amplitudes are substituted for the Rayleigh–Schrödinger coefficients. In essence, the coupled-cluster [83] solution for the ground state

$$|0\rangle = e^{T}|HF\rangle \tag{3.6}$$

with T being

$$T = T_1 + T_2 \tag{3.7}$$

in which

$$T_1 = \sum_{m\alpha} t_{\alpha}^{m} a_{m}^{+} a_{\alpha} \tag{3.8}$$

$$T_2 = \frac{1}{4}\sum_{mn\alpha\beta} t_{\alpha\beta}^{mn} a_{m}^{+} a_{n}^{+} a_{\alpha} a_{\beta} \tag{3.9}$$

Here, greek indices denote orbitals that are occupied in the Hartree–Fock ground state $|HF\rangle$ whereas roman indices label unoccupied orbitals; a_m^+ and a_α are creation and annihilation operators, respectively.

In an extension of SOPPA with coupled-cluster singles and doubles amplitudes (CCSDPPA), the latest version of which is denoted SOPPA(CCSD) [84], we replace first-order Rayleigh–Schrödinger doubles coefficients with amplitudes $t_{\alpha\beta}^{mn}$ and second-order Rayleigh–Schrödinger singles coefficients with amplitudes t_α^m. A justification of this practice is that first-order Rayleigh–Schrödinger coefficients are an approximation of least order to amplitudes $t_{\alpha\beta}^{mn}$, i.e., amplitudes obtained in the first iteration of the iterative solution required to solve the coupled-cluster equation [83]. By using converged values of these amplitudes, we include effects of double excitation to infinite order in perturbation theory. The method SOPPA(CCSD) remains basically a second-order theory in the sense that contributions to $\langle\langle A; B\rangle\rangle_\omega$ in third order are lacking [82], but it accounts for electronic correlation that is important especially in a system with near-degeneracy; in our experience, in many cases it improves performance relative to the SOPPA method. The SOPPA(CCSD) method has been applied to the calculation of g factors [26].

As we achieve matrices t, s, P, and Q are calculated from one- and two-electron integrals, a method to evaluate molecular properties that circumvents a sum over states; a computational implementation of this method is described elsewhere [78,84,85].

The response function in Eq. (3.3) might also be evaluated with a MCSCF reference function rather than with a perturbative approach according to SOPPA-like approximations. The former approach is denoted with acronyms CASSCF (SCF with complete active space) and RASSCF (SCF with restricted active space), depending on the choice made for configurations included in the reference function in addition to the SCF configuration, i.e., in addition to the one included in the RPA or CHF method. In the limit in which all possible configurations in a given basis set are included, both methods become the full configuration, interaction (CI) method. The CASSCF, RASSCF, and full CI methods have all been applied to calculation of g factors; results are reported in the Appendix to the present article.

C. Second-Derivative Methods

To calculate g_r^e using Eq. (3.1), it is necessary to compute the energy contribution to second order in B and J in both the wave function and the Hamiltonian, expressed formally as

$$\begin{aligned}\left(\frac{\partial^2 E^e}{\partial \vec{B}\partial \vec{J}}\right)_{\vec{B},\vec{J}=0} &= \left\langle \Psi \left| \left(\frac{\partial^2 H}{\partial \vec{B}\partial \vec{J}}\right)_{\vec{B},\vec{J}=0} \right| \Psi \right\rangle \\ &+ \left\langle \left(\frac{\partial \Psi}{\partial \vec{B}}\right)_{\vec{B}=0} |H| \left(\frac{\partial \Psi}{\partial \vec{J}}\right)_{\vec{J}=0} \right\rangle + \left\langle \left(\frac{\partial \Psi}{\partial \vec{J}}\right)_{\vec{J}=0} |H| \left(\frac{\partial \Psi}{\partial \vec{B}}\right)_{\vec{B}=0} \right\rangle \\ &+ \left\langle \left(\frac{\partial \Psi}{\partial \vec{B}}\right)_{\vec{B}=0} \left| \left(\frac{\partial H}{\partial \vec{J}}\right)_{\vec{J}=0} \right| \Psi \right\rangle + \left\langle \left(\frac{\partial \Psi}{\partial \vec{J}}\right)_{\vec{J}=0} \left| \left(\frac{\partial H}{\partial \vec{B}}\right)_{\vec{B}=0} \right| \Psi \right\rangle \\ &+ \left\langle \Psi \left| \left(\frac{\partial H}{\partial \vec{B}}\right)_{\vec{B}=0} \right| \left(\frac{\partial \Psi}{\partial \vec{J}}\right)_{\vec{J}=0} \right\rangle + \left\langle \Psi \left| \left(\frac{\partial H}{\partial \vec{J}}\right)_{\vec{J}=0} \right| \left(\frac{\partial \Psi}{\partial \vec{B}}\right)_{\vec{B}=0} \right\rangle \\ &+ \left\langle \left(\frac{\partial^2 \Psi}{\partial \vec{B}\partial \vec{J}}\right)_{\vec{B},\vec{J}=0} |H| \Psi \right\rangle + \left\langle \Psi |H| \left(\frac{\partial^2 \Psi}{\partial \vec{B}\partial \vec{J}}\right)_{\vec{B},\vec{J}=0} \right\rangle \qquad (3.10)\end{aligned}$$

According to Eq. (1.5),

$$\left(\frac{\partial H}{\partial B_\alpha}\right)_{\vec{B}=0} = \frac{e}{2m_e}\sum_i l_{i,\alpha}(\vec{R}_o) \qquad (3.11)$$

and to Eqs. (1.4) and (1.19),

$$\left(\frac{\partial H}{\partial J_\alpha}\right)_{\vec{J}=0} = -\frac{m_e}{e}\sum_i l_{i,\alpha}(\vec{R}_{\mathrm{CM}})I^{-1} \qquad (3.12)$$

Replacing $\frac{\mu_N}{\hbar}\boldsymbol{g}_r\vec{J}$ in Eq. (1.31) with the induced magnetic moment [Eq. (1.15)], and making use of Eq. (1.22), we reduce the second derivative in Eq. (3.10) to

$$\begin{aligned}\left(\frac{\partial^2 H}{\partial \vec{B}\partial \vec{J}}\right)_{\vec{B},\vec{J}=0} &= \frac{1}{2}\sum_i((\vec{R}_o - \vec{R}_{\mathrm{CM}}) \\ &\quad \cdot (\vec{r}_i - \vec{R}_{\mathrm{CM}})\delta_{\alpha\beta} - (r_{i,\alpha} - R_{\mathrm{CM},\alpha})(R_{o,\beta} - R_{\mathrm{CM},\beta})) \qquad (3.13)\end{aligned}$$

First and second derivatives of a wave function can be computed using standard first- and second-derivative techniques [86,87]; these techniques are available for both correlated and uncorrelated wave functions and have been applied to calculations of rotational g tensors at both uncorrelated [88] and multiconfigurational self-consistent field levels of approximation [89].

Although these calculations might be performed using standard atomic basis sets, calculations of magnetizabilities [90] indicate that operator expressions involving operators for electronic angular momentum such as

Eqs. (3.11) and (3.12) show slow convergence with standard basis sets and that convergence can be accelerated considerably with perturbation-dependent basis sets. In the case of the rotational g factor the natural perturbation-dependent basis set consists of functions called [88] rotational London orbitals; these functions depend on both magnetic and rotational perturbations. By analogy with ordinary London orbitals [91] or gauge-including atomic orbitals [92,93],

$$\phi_\mu^{LAO}(\vec{r}_i - \vec{R}_\mu) = e^{-i\vec{A}_\mu^B \cdot \vec{r}_i} \chi_\mu(\vec{r}_i - \vec{R}_\mu) \tag{3.14}$$

rotational London orbitals are defined as

$$\phi_\mu^{RLAO}(\vec{r}_i - \vec{R}_\mu) = e^{-i(\vec{A}_\mu^B + \vec{A}_\mu^J) \cdot \vec{r}_i} \chi_\mu(\vec{r}_i - \vec{R}_\mu) \tag{3.15}$$

in which [see Eqs. (1.2) and (1.19)]

$$\vec{A}_\mu^B = \frac{1}{2} \vec{B} \times (\vec{R}_\mu - \vec{R}_o) \tag{3.16}$$

$$\vec{A}_\mu^J = -\frac{m_e}{e} \vec{J} \times \vec{R}_\mu \boldsymbol{I}^{-1} \tag{3.17}$$

$\vec{R}_\mu$ is the position of a Gaussian function χ_μ centered on an atom. Besides improved convergence of the basis set, use of rotational London orbitals eliminates dependence of computed rotational g tensors on the gauge origin: g_r becomes independent of $\vec{R}_o$ [see Eq. (1.22)].

With the derivative technique, the simple relationship between g_r^e and ξ^p [Eq. (1.26)] is inapplicable because the paramagnetic contribution to magnetizability, calculated with London orbitals [94], is poorly defined. The earliest attempt to establish such a relation made use of a so-called natural connection between the standard (unperturbed) basis set and perturbed London orbitals [95]. A disadvantage of this approach is that only in the limit of a complete basis set is the conventional relationship between a rotational g tensor and the paramagnetic contribution to magnetizability obtained. Using rotational London orbitals one finds, however, from comparison of expressions for g_r^e [88] and the total magnetizability computed using London orbitals [94] that

$$g_r^{e,RLAO} = -4m_p(\xi^{LAO} - \xi^d(\vec{R}_{\rm CM}))\boldsymbol{I}^{-1} \tag{3.18}$$

Eqs. (3.11) and (3.12) show slow convergence with standard basis sets and that convergence can be accelerated considerably with perturbation-dependent basis sets. In the case of the rotational *g* factor the natural perturbation-dependent basis set consists of functions called [88] rotational London orbitals; these functions depend on both magnetic and rotational perturbations. By analogy with ordinary London orbitals [91] or gauge-including atomic orbitals [92,93],

$$\phi_{\mu}^{LAO}(\vec{r}_i - \vec{R}_{\mu}) = e^{-i\vec{A}_{\mu}^{B}\cdot\vec{r}_i}\chi_{\mu}(\vec{r}_i - \vec{R}_{\mu}) \tag{3.14}$$

rotational London orbitals are defined as

$$\phi_{\mu}^{RLAO}(\vec{r}_i - \vec{R}_{\mu}) = e^{-i(\vec{A}_{\mu}^{B}+\vec{A}_{\mu}^{J})\cdot\vec{r}_i}\chi_{\mu}(\vec{r}_i - \vec{R}_{\mu}) \tag{3.15}$$

in which [see Eqs. (1.2) and (1.19)]

$$\vec{A}_{\mu}^{B} = \frac{1}{2}\vec{B} \times (\vec{R}_{\mu} - \vec{R}_{o}) \tag{3.16}$$

$$\vec{A}_{\mu}^{J} = -\frac{m_e}{e}\vec{J} \times \vec{R}_{\mu}\boldsymbol{I}^{-1} \tag{3.17}$$

$\vec{R}_{\mu}$ is the position of a Gaussian function χ_{μ} centered on an atom. Besides improved convergence of the basis set, use of rotational London orbitals eliminates dependence of computed rotational *g* tensors on the gauge origin: g_r becomes independent of $\vec{R}_o$ [see Eq. (1.22)].

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$$g_r^{e,RLAO} = -4m_p(\xi^{LAO} - \xi^{d}(\vec{R}_{\mathrm{CM}}))\boldsymbol{I}^{-1} \tag{3.18}$$

in which $\xi^d(\vec{R}_{\mathrm{CM}})$ denotes a conventional expression [see Eq. (1.9)] for the diamagnetic contribution to magnetizability. This expression has the same structure as Eq. (1.26) and coincides with the relationship obtained from a sum over states in the limit of a complete basis set.

IV. APPLICATIONS

A. Sign of Permanent Electric Dipolar Moment

Apart from intrinsic importance of the rotational g factor as a characteristic molecular property, perhaps the first application of this parameter was its use in determining not only an approximate magnitude but more especially the sign of a permanent molecular electric dipolar moment [24] with respect to a molecular axis. As the Stark effect in microwave spectra of linear molecules, being quadratic in both electric field and dipolar moment, yields only a magnitude of electric moment with an accuracy acceptable for many purposes, this application of the Zeeman effect provided information of chemical interest. Magnetic susceptibility is independent of an origin of coordinates. For an isotopic substitution that displaces the center of molecular mass a distance $(R'_{\mathrm{CM}} - R_{\mathrm{CM}})$ along the internuclear (or z-) axis, the moment of inertia I and rotational g factor g_r of a linear molecule become altered to I' and g'_r, respectively. Then the z-component of the electric moment d_z at R_e of a net electrically neutral molecule is estimated from a relation

$$d_z = \frac{e}{2m_p} \frac{\left(Ig_r - I'g'_r\right)}{\left(R'_{\mathrm{CM}} - R_{\mathrm{CM}}\right)} \tag{4.1}$$

This relation is equivalent to that in Eq. (1.48). The numerator of Eq. (4.1) is typically a small quantity; the resulting magnitude, and even the sign, of d_z is thus susceptible to uncertainty propagated from error of measurement of g_r. Great care must be taken in application of this equation to experimental g factors because it refers to a particular internuclear distance [see Eq. (1.48)]. Apart from the method described in Section II.E, experimentally determined g factors are for a vibration–rotational state $|\, v, J\rangle$. Therefore, the g factors of both isotopic variants must be extrapolated to the same internuclear distance before this equation can become applicable. Inaccuracies in such extrapolation can produce large errors in electric dipolar moments deduced from Eqs. (1.48) and (4.1), as in the case of ArH^+ [25].

The first application of this method was made to carbon oxide, in which the authors purportedly deduced a polarity $^-\mathrm{CO}^+$ [96]; because the sign of

g_r was not determined but deduced to be negative on the basis of supposed ratios of atomic masses, the proof was incomplete. Subsequent analysis of those ratios indicated that experimental values were equally compatible with g_r of either sign [97]. The correct sign was eventually confirmed to be negative in a direct experiment with a molecular beam and magnetic resonance [55].

For chlorine fluoride, the result of such application of a Zeeman effect in microwave spectra to determine the rotational g factor yielded a polarity $^{-}ClF^{+}$ [98] that was not only contrary to chemical intuition but also in disagreement with results of quantum–chemical computations [99]. After an incredulous reception and further calculations [100], repeated experiments in the same laboratory seemed to confirm the result [101], but subsequent experiments elsewhere provided first indirect [102] (by means of experiments on a molecular beam with electric resonance in the microwave spectrum of the complex HF–ClF) and then direct (with the same method on ClF [103]) evidence of error in the original deduction [98,101]. A reason suggested for the error was that a value of g_r was too small because unresolved hyperfine structure distorted the shape of the spectral lines. Likewise, for molecules with many rotational states and for strong coupling between a nuclear spin and rotational angular momentum, the method combining magnetic resonance and a molecular beam fails to yield reliable results for g_r [40,42].

For hydride ions of noble-gas atoms, the sign of g_r appears unsettled at present. For HeH^+, g_r is calculated to be positive [68,104,105]. For NeH^+, only a calculation is reported [104,105], one which predicts a positive sign. For ArH^+, both experiment [106] and calculations [25,104,105] yield a positive sign, but aspects of analysis of experimental data to deduce a value of electric dipolar moment with respect to the center of mass are questionable. For XeH^+, a positive value is reported [104,105,107], but consideration of the experiment indicates that only a magnitude can be estimated from broadening of spectral lines. For KrH^+, g_r is assigned a negative value [108] on the basis that this sign is required to yield a calculated sign of electric dipolar moment [109], but subsequent calculations [104,105] predict the opposite sign while reproducing the numerical value. Further calculations and experiments on molecules in this family are clearly in order; comparisons with nominally isoelectronic halogen hydrides are likely to yield insight into aspects of interpretation of both calculations and experiments.

The method to determine g_r from measurement of frequencies of pure rotational and vibration–rotational spectral transitions [110] can concurrently yield a sign and rough magnitude of d_z. For GaH, although $t_0^H = -3.17042 \pm 0.00062$ is satisfactorily evaluated [defined in Eq. (2.23)], the precision of $t_0^{Ga} = -3.73 \pm 0.34$ is such that the difference between t_0^H and t_0^{Ga} is less than twice the standard error of the latter quantity. On reference to Eqs. (2.29) through (2.31), it is evident that, under a condition that $M_{Ga} \gg M_H$, $g_r^{irr}(R_e)$ and $g_r(R_e)$ are accurately deduced but d_z is essentially undefined. This value, $g_r = -3.22 \pm 0.10$ for $^{69}Ga^1H$ [110], conforms acceptably with values in the range from -3.444 to -2.942, calculated with polarization–propagator approximations at various levels [26].

Analysis of only frequency data, including both pure rotational and vibration–rotational transitions of multiple isotopic variants, yielded polarities $^+GeS^-$ [111], $^+GeSe^-$ (Ogilvie, unpublished results) and $^+BrCl^-$ [112] of these species. The associated values of $g_r(R_e)$ agree roughly with those of g_r of the former two species measured with the Zeeman effect in microwave spectra and with magnitudes of d_z with the Stark effect of all three species; no value of g_r from experiment on BrCl is reported. In all cases precisions of values of g_r and d_z according to this approach are much poorer than those of values derived with the use of magnetic and electric fields, but their signs arise directly, rather than indirectly from a Zeeman effect and not at all from a quadratic Stark effect.

B. Experimental Magnetizability

According to earlier discussion in Section I.C.2, the electronic contribution to the rotational g factor is seen to be related to the paramagnetic contribution of the magnetizability [Eq. (1.26)]. The total perpendicular component of the magnetizability of a diatomic molecule can thus be obtained from measured rotational g factors and a calculated diamagnetic contribution [Eqs. (1.28) and (1.29)]. This relation is applied [113] to deduce experimental evidence for the paramagnetism of AlH and BH. The value $g_r(R_e) = -2.7 \pm 0.5$ for $^{27}Al^1H$ was poorly determined from available vibration–rotational spectra [113], mainly because lack of data for an isotope of Al produces large correlations between parameters in a fit of spectral data. The calculated value is -3.2 [113]. A previous estimate $g_r(R_e) = -2.25 \pm 0.25$, the first derivation of a value of g_r from spectral data of only vibration–rotational wavenumbers [114], resulted from analysis of spectral data [115] obtained under conditions of resolution and precision both of which were poorer than those present in subsequent experiments [116]. Calculation of magnetizability of AlH from the later experimental result of g_r, with a calculated value of $\xi_\perp^d$, yielded a conclusion [113] that the perpendicular component of total magnetizability was marginally positive, indicating the paramagnetic character of that component, even though total magnetizability has diamagnetic character. This evidence, even if indirect, is the first from experiment to support the prediction [117–127], from quantum–chemical computations, that BH, nominally isoelectronic with AlH (with both Al and B in group 13 of the periodic chart of chemical elements), has a paramagnetic ground electronic state despite its symmetry class being $^1\Sigma^+$.

C. Evaluation of Adiabatic and Nonadiabatic Effects

Adiabatic and nonadiabatic effects have no true physical origin; they arise because treatment of a molecule with formal separation of nuclear and electronic motions is approximate. Because these motions are coupled and because electrons follow imperfectly one or other nucleus, ratios of spectral parameters deviate from ratios of atomic masses or reduced atomic masses to simple powers [96]. Adiabatic effects reflect a condition that internuclear potential energy depends not only on static coulombic interactions but also, through reactions of nuclear motions, on electronic motions that occur in an attempt to conserve momentum; thus these effects depend on inverse nuclear masses [32]. Nonadiabatic effects become introduced empirically into an effective Hamiltonian for nuclear motion as dependences of reduced atomic masses on internuclear distance, in kinetic energy of nuclei along or perpendicular to the line between their centers. During analysis of spectral data comprising transition frequencies of great precision, one has perforce to employ atomic masses, known to comparable precision [128], instead of nuclear masses because the latter are almost invariably much less well characterized.

A practical way to investigate these adiabatic and nonadiabatic effects involves term coefficients Z_{kl}^r and Z_{kl}^v of each atomic type, introduced in Eq. (2.19). As mentioned above, experimental evidence represented symbolically in these quantities is in general inadequate to yield three radial functions involving coefficients u_j, t_j, and s_j of each atomic type. Even when the functions number only five in total by means of representation in terms of $g_r^{irr}(R)$ and $g_v^{irr}(R)$ of each atomic type plus a function for electric dipolar moment, insufficiency remains. Although algorithms generally applicable to calculate adiabatic effects, especially their dependence on internuclear distance, are either lacking or little utilized and although those to calculate nonadiabatic vibrational effects are scarcely contemplated at present, methods intended to calculate nonadiabatic rotational effects through the rotational g factor are well established. With a combination of radial dependences in $g_r(R)$ and $d_z(R)$ thereby known from calculation, an analysis of experimental data from spectral frequencies can hence, in principle, yield unambiguously the separate adiabatic and nonadiabatic vibrational effects. Such quantum–chemical calculations are most readily undertaken for molecules having few electrons, for reasons of duration of computation at each particular internuclear distance and of avoiding inaccuracy due to partial neglect of electronic correlation and to relativistic effects.

As an instance of this approach, computations of $g_r(R)$ and $d_z(R)$ of LiH provided constraints for values of t_j^{Li} and t_j^{H} during fits of spectral data of LiH [129]. Because available spectral data possessed only moderate quality and quantity, values only of u_j^{Li}, $j = 1$ and 2, and of u_j^{H}, $1 \leq j \leq 3$, were well defined pertaining to adiabatic effects, as were those of s_0^{Li} and s_0^{H} pertaining to nonadiabatic vibrational effects. That the latter two values reproduced approximately the pertinent value of $\partial d_z/\partial z$ according to relations [32] analogous to Eq. (2.34) indicates that analysis to be self-consistent. A novel result of this analysis is that for LiH adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects have comparable magnitudes, signifying comparable contributions to vibration–rotational energies. Further analysis (Ogilvie, unpublished results) based on improved spectral data [130] confirms this conclusion.

D. Accurate Equilibrium Lengths of Chemical Bonds

As a molecule in an eigenstate with respect to electronic and nuclear motion has, rigorously, extension in neither space nor time [131], and as the effective bond length for a molecule in a particular vibrational state depends not only on the vibrational quantum number but also on the experimental method (which produces expectation values $\langle v|R^{-2}|v\rangle$, $\langle v|R^{-3}|v\rangle$, etc.) a meaningful bond length arises only through a theoretical procedure with a separate treatment of electronic and nuclear motions. The appropriate length, designated R_e, is thus an equilibrium value for a hypothetical state that lacks residual (or zero-point) energy and that is formally independent of nuclear (or isotopic) mass. Well developed methods to approach this value from experiment rely essentially on extrapolation from vibrational states with $v \geq 0$ for a particular isotopic variant, but the value R_e formally obtained in a conventional calculation of molecular electronic structure can be reproduced from experimental data in principle only on taking into account both adiabatic effects, represented specifically in $u_1^{a,b}$ in Eq. (2.22) and nonadiabatic rotational effects, represented specifically in $t_0^{a,b}$ in Eq. (2.23); these specific members of sets of coefficients u_j and t_j are discerned according to particular parameters in analytic expressions for $Z_{0,1}^{v}$ and $Z_{0,1}^{r}$ in Eq. (2.19) [6,57]. In practice the discrepancy between a value of R_e from a quantum–chemical calculation of molecular electronic structure and the corresponding value from global analysis of infrared spectra of compounds having multiple isotopic variants is typically about 1000 times the uncertainty of R_e arising from propagation of error of frequency measurements in contemporary analyses of precise vibration–rotational spectra when these adiabatic and nonadiabatic rotational effects are included.

Conversely, for molecules having few electrons, for which quantum–chemical computations might seek to attain the ultimate precision of the underlying theory, adiabatic and nonadiabatic corrections must be incorporated before comparison with precise experimental values of R_e becomes meaningful. Accuracies $\approx 2.5 \times 10^{-13}$ m are currently claimed for conventional calculations [132], with no material improvement from almost a decade earlier [133]; for a bond length R_e about 10^{-10} m, typical of C–H or O–H, adiabatic effects are of the order $R_e m_e/M_a$, hence at most 5×10^{-14} m for a molecule containing ^{1}H. Furthermore, adiabatic and nonadiabatic effects show comparable orders of magnitudes for light molecules [129], although adiabatic effects appear relatively to decrease for more massive molecules [134]. Significant improvement of accuracy of conventional calculations must thus be generally attained before corrections for adiabatic and nonadiabatic effects require attention [135].

V. DISCUSSION AND CONCLUSION

A. Physical Interpretation of Rotational g Factor

Espe estimated an electronic contribution to the rotational g factor of H_2 with a relation of a form [136]

$$g_r^e = \langle \Psi_0^{(0)} \mid \sum_i (x_i^2 + y_i^2) \mid \Psi_0^{(0)} \rangle \frac{\left[\frac{\langle \Psi_0^{(0)} | \sum_i (x_i^2 - y_i^2) | \Psi_0^{(0)} \rangle}{\langle \Psi_0^{(0)} | \sum_i (x_i^2 + y_i^2) | \Psi_0^{(0)} \rangle} \right]^2}{\mu R^2} \tag{5.1}$$

having a structure similar to that of Eq. (1.49). Here the first factor $\langle \Psi_0^{(0)} \mid \sum_i (x_i^2 + y_i^2) \mid \Psi_0^{(0)} \rangle$ arises because the effectiveness of each electron in creating a magnetic dipolar moment depends on the square of its distance from the internuclear axis; the amount of rotation imparted to electrons by nuclei depends on asymmetry of the electronic cloud, measured according to this approximation with the normalized molecular electric quadrupolar moment $[\langle \Psi_0^{(0)} \mid \sum_i (x_i^2 - y_i^2) \mid \Psi_0^{(0)} \rangle / \langle \Psi_0^{(0)} \mid \sum_i (x_i^2 + y_i^2) \mid \Psi_0^{(0)} \rangle]^2$, and the rotational velocity of the nuclei depends on their moment of inertia, μR^2. This estimate agrees reasonably well with the experimental value of g_r for H_2 when the nuclear contribution is taken into account, by means of Eq. (1.27).

Although properties of an electronic distribution depend on all electrons, the portion of electronic charge near a nucleus might thus contribute little to g_r because a factor $\langle \Psi_0^{(0)} \mid \sum_i (x_i^2 + y_i^2) \mid \Psi_0^{(0)} \rangle$ appears in the numerator of the above relation. For dialkali molecules Li_2 to Cs_2, Brooks et al. [137,138]