Calculated Rotational and Vibrational gFactors of LiH X ${}^{1}\Sigma^{+}$ and Evaluation of Parameters in Radial Functions from Rotational and Vibration-Rotational Spectra

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ABSTRACT: The vibrational *g* factor, that is, the nonadiabatic correction to the vibrational reduced mass, of LiH has been calculated for internuclear distances over a wide range. Based on multiconfigurational wave functions with a large complete active space and an extended set of gaussian type basis functions, these calculations yielded

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also the rotational g factor, the electric dipolar moment, and its gradient with internuclear distance for LiH in its electronic ground state X ${}^{1}\Sigma^{+}$. The vibrational *g* factor g_{v} exhibits a pronounced minimum near internuclear distance $R = 3.65 \times 10^{-10}$ m; the derivative of electric dipolar moment and the nonadiabatic matrix element coupling the electronic ground state to the first electronically excited state exhibit extrema near the same location that is also near the avoided crossing of the curves for potential energy for the electronic ground state and excited state A ${}^{1}\Sigma^{+}$. The irreducible contribution $g_{r}^{irr}(R)$ to the rotational g factor increases monotonically over the calculated domain, whereas the irreducible contribution $g_v^{irr}(R)$ to the vibrational g factor has a minimum at the same location as that of g_{y} itself. From these calculated radial functions, we derived values of the rotational g factor and electric dipolar moment for LiH in vibrational states v = 0 and 1, and the corresponding rotational dependences, in satisfactory agreement with experimental values. These calculated data of rotational g factor served as constraints in new fits of 1000 vibration-rotational spectral data of LiH in four isotopic variants, which yield estimates of adiabatic corrections for comparison with published data and of the vibrational g factor for comparison with our calculated results. ©2010 Wiley Periodicals, Inc. Int J Quantum Chem 111: 736-752, 2011

Key words: rotational *g* factor; vibrational *g* factor; nonadiabatic reduced mass; spectral fitting; LiH

1. Introduction

A research interest of David M. Bishop was highly accurate calculations of properties of atoms and diatomic molecules. Among the latter, LiH figured in at least five reports [1–5], of which two [1, 2] were concerned with adiabatic potential energy surfaces for states X ${}^{1}\Sigma^{+}$ and A ${}^{1}\Sigma^{+}$. Our contribution to this memorial issue is thus appropriately a combined theoretical and experimental investigation of nonadiabatic contributions to vibration-rotational spectra of LiH in the electronic ground state.

According to computational spectrometry [6], we developed a procedure whereby one applies the results of quantum-chemical calculations as constraints within analyses of wavenumber data of lines in infrared spectra measured at high resolution; we applied this approach first to spectra of LiH [7]. A conventional mechanical model might serve as a basis of interpreting such spectra in terms of the nuclear vibration and rotation of free diatomic molecules in a gaseous sample at small density: Two atomic centers A and B, regarded as point masses at distance R apart in a particular molecule AB, oscillate about the center of mass along an interatomic vector and rotate about that center, apart from translation of the entire molecule within an enclosing vessel that produces no

discernible spectral effect of interest here. A corresponding primitive Hamiltonian thereby comprises three terms,

$$H(R) = \frac{1}{2}\frac{\hat{p}^2}{\mu} + \frac{\hbar^2}{2\mu R^2}J(J+1) + V(R)$$
(1)

that pertain to the kinetic energy of relative atomic motion along the interatomic vector, the kinetic energy of relative motion perpendicular to that axis, or molecular rotation, and interatomic potential energy V(*R*), respectively, all regarded as mechanical effects. For a reduced mass μ of a neutral diatomic molecule in terms of two atomic masses $M_{\rm a}$ and $M_{\rm b}$,

$$\frac{1}{\mu} = \frac{1}{M_{\rm a}} + \frac{1}{M_{\rm b}}$$
 (2)

 \hat{p} denotes the relative linear momentum conjugate to *R*; the angular momentum is $\hbar\sqrt{J(J+1)}$. Because a diatomic molecule contains two atomic nuclei and their associated electrons, rather than structureless or spherically symmetric atoms, and because electrons follow imperfectly the motion of one or other nucleus in a classical sense, the former Hamiltonian is inadequate to explain infrared spectra recorded at the greatest contemporary spectral resolution; we have thus recourse to an extended effective Hamiltonian [8] for nuclear motion applicable to an electronic state of symmetry class ${}^{1}\Sigma^{+}$ as follows.

$$H_{\rm eff}(R) = \frac{1}{2\mu} \hat{p} \left[1 + g_v(R) \frac{m_{\rm e}}{m_{\rm p}} \right] \hat{p} + \frac{\hbar^2 J(J+1)}{2\mu R^2} \left[1 + g_r(R) \frac{m_{\rm e}}{m_{\rm p}} \right] + V(R) + \Delta V(R) \quad (3)$$

This formula contains terms further to those of Eq. (1) in recognition of the existence of extra-mechanical effects [9] of two types [10]: adiabatic corrections pertain to theoretical expressions that involve expectation values of quantum-mechanical operators within a particular electronic state of interest, in practice, the electronic ground state; nonadiabatic effects involve matrix elements of the same or other operators connecting that electronic ground state with electronically excited states, as follows. A radial function $g_r(R)$ for the rotational g factor in a term for the kinetic energy of rotation has nuclear and electronic contributions; for a molecule with electronic ground state of class Σ , the latter contribution involves matrix elements to electronically excited states of symmetry class Π and constitutes the nonadiabatic contribution to the rotational reduced mass. Another radial function $g_v(R)$ for the vibrational g factor in the term for the kinetic energy of vibration likewise contains contributions from atomic nuclei and electrons; this contribution involves matrix elements to electronically excited states of the same class Σ , and constitutes the nonadiabatic contribution to the vibrational reduced mass. According to convention, the radial functions for both rotational and vibrational g factors have as multiplicand a ratio m_e/m_p of electronic and protonic rest masses. From an experimental point of view, the splitting of lines in a pure rotational spectrum on subjection of a gaseous sample to a magnetic field is a direct manifestation of the rotational g factor, but g_v is experimentally accessible through no known magnetic effect of low order [11]. An additional term $\Delta V(R)$ in the effective Hamiltonian is purely an artifact of an approximate theoretical treatment according to which electronic and nuclear motions are treated separately, which also generates V(R) as the electronic energy at internuclear distance R. This correction term $\Delta V(R)$, which takes partly into account the fact that internuclear potential energy V(R) would otherwise have a small dependence on nuclear mass, includes both expectation values of operators in the ground electronic state: thus, adiabatic corrections, with a relative dependence on ratio m_e/M of electronic and nuclear masses to the first power, and matrix elements connecting the electronic ground state with electronically excited states [8, 10]; thus, further nonadiabatic effects, but with a relative dependence on a ratio $m_{\rm e}/M$ to a power greater than unity. We thus express $\Delta V(R)$ as $\Delta V_{ad}(R) + \Delta V_{nad}(R)$, but neglect $\Delta V_{\rm nad}(R)$ because its dependence on ratio m_e/M with exponent 3/2 or larger makes it much smaller than retained terms [8]; its effects in our collected molecular spectra of LiH would be much smaller than the experimental uncertainty of wavenumber or frequency measurements. All these terms due to extra-mechanical effects are expressible as sums of contributions from separate atomic centers A and B [8].

Hence, $\mu \left(1 + g_v(R) \frac{m_e}{m_p}\right)^{-1}$ in Eq. (3) represents an effective reduced mass for vibration dependent on internuclear separation *R*, and $\mu \left(1 + g_r(R) \frac{m_e}{m_p}\right)^{-1}$ represents an analogous effective reduced mass for rotation [11]; thereby $g_v(R)$ and $g_r(R)$ absorb all effects of the deviation of the distribution of electronic charge from a spherical form centered on an atomic nucleus that would correspond to the condition of an isolated, electrically neutral atom as part of an electrically neutral diatomic molecule.

For a diatomic molecule of a particular isotopic variant *i* in an electronic state of symmetry class ${}^{1}\Sigma^{+}$, we express the spectral terms, or energies divided by *hc*, of this effective Hamiltonian [9],

$$E_{vJ}^{i} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \left(Y_{kl} + Z_{kl}^{a,v} + Z_{kl}^{a,r} + Z_{kl}^{b,v} + Z_{kl}^{b,r} \right) \\ \left(v + \frac{1}{2} \right)^{k} \left[J(J+1) \right]^{l} \quad (4)$$

in which appear vibrational quantum number v and rotational quantum number J in the absence of other pertinent contributions to total molecular angular momentum. The principal coefficients Y_{kl} reflect a presence of terms for mechanical effects in a primitive Hamiltonian, Eq. (1); auxiliary term coefficients Z_{kl}^a and Z_{kl}^b represent additional terms resulting from extra-mechanical effects in an effective Hamiltonian, Eq. (3), for atomic centers of types A and B separately. Following Dunham's algebraic approach [12] as extended by van Vleck [10] and others [13], we form radial functions as polynomials in variable z [14, 15]; the latter

quantity denotes a reduced and dimensionless displacement of instantaneous internuclear separation R from equilibrium internuclear distance R_{er}

$$z = 2\frac{R - R_{\rm e}}{R + R_{\rm e}} \tag{5}$$

As parameters besides R_e , we use coefficients of *z* in four radial functions [9], with coefficients c_i for potential energy independent of mass,

$$V(R) \to V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{\infty} c_j z^j \right) \tag{6}$$

coefficients s_j for nonadiabatic vibrational effects and the associated nuclear contribution that pertain [16] to the vibrational *g* factor, g_{v} ,

$$g_{\rm v}(R) \to g_{\rm v}^a(z) + g_{\rm v}^b(z) = m_{\rm p} \left[\sum_{j=0}^{\infty} \frac{s_j^a z^j}{M_{\rm a}} + \sum_{j=0}^{\infty} \frac{s_j^b z^j}{M_{\rm b}} \right]$$
 (7)

coefficients t_j for nonadiabatic rotational effects and the associated nuclear contribution that pertain [17] to the rotational *g* factor, g_{r} ,

$$g_{\rm r}(R) \to g_{\rm r}^a(z) + g_{\rm r}^b(z) = m_{\rm p} \left[\sum_{j=0}^{\infty} \frac{t_j^a z^j}{M_{\rm a}} + \sum_{j=0}^{\infty} \frac{t_j^b z^j}{M_{\rm b}} \right]$$
(8)

and coefficients u_i for adiabatic corrections [9]:

$$\Delta V_{\rm ad}(R) \to m_{\rm e} \left[\sum_{j=0}^{\infty} \frac{u_j^a z^j}{M_{\rm a}} + \sum_{j=0}^{\infty} \frac{u_j^b z^j}{M_{\rm b}} \right] \tag{9}$$

Although extra-mechanical effects taken explicitly into account in our effective Hamiltonian, Eq. (3), number three, only two contributions to auxiliary term coefficients are experimentally distinguishable for atoms of each type A or B separately through use of isotopic variants; we denote these as Z_{kl}^{v} for vibration-rotational terms that involve parameters in $\Delta V_{ad}(z)$ and $g_v(z)$, and as Z_{kl}^{r} for further rotational terms that involve parameters in $g_v(z)$ and $g_r(z)$ [9]. The physical basis of this criterion is that these extra-mechanical effects are shown to express a dependence on individual masses of atoms of each type [8], and the nature of these dependences makes them separable. It is thus in general impracticable to evaluate multiple parameters of three types s, t, and u in complete sets up to a particular order for atomic centers of types either A or B in a heteronuclear diatomic molecule from only data of frequencies and wavenumbers of spectral transitions for samples of a diatomic molecular compound in the absence of an external field.

For that reason [6], in preceding work, we combined calculated values of the rotational g factor and electric dipolar moment p as a function of internuclear separation to evaluate coefficients of types t_i^a and t_i^b , thereby simulating experimental data prospectively derivable from extensive experimental application of Zeeman and Stark effects, respectively; we constrained the resulting values of those coefficients while adjusting values of parameters of types c_i , s_i^a , s_i^b , u_i^a , and u_i^b to reproduce satisfactorily experimental data of frequency and wave numbers, first for LiH [7] and subsequently for other diatomic molecular species AlH [18] and CO [19]. To assess the significance of these deduced radial functions $g_v(R)$ and $\Delta V_{ad}(R)$ in the present work, we compare them with our calculations for the vibrational g factor and with adiabatic corrections reported by Bishop and Cheung [1]. For the rotational g factor, reviewed elsewhere [20], the experimental, theoretical, and computational aspects are well established, unlike the vibrational g factor that we here investigate in some detail.

In our original joint work on LiH [7], we fitted 12 values of rotational $g_r(R)$ factor and electric dipolar moment p(R) for ⁷Li¹H in a domain $R/10^{-10}$ m = [1.17, 2.18], or |z| < 0.309, to generate, through coefficients t_i^{Li} and t_i^{H} in Eq. (8), a radial function $g_r(z)$; we applied the latter in fitting 557 wavenumbers and frequencies of vibration-rotational and pure rotational spectral transitions. A plot of this function $g_{\rm r}(R)$ yields a curve varying monotonically within that domain, eventually approaching zero asymptotically at distances for $R \gg R_e = 1.5949 \times 10^{-10}$ m; this behavior is regular, and typical of this function for neutral diatomic molecules for which these calculations have been performed [20-24]. In the present work in which the fitted spectral data number 1000, we increased the domain of these calculations to R/ 10^{-10} m = [1.05, 10.0]; we found a similar behavior, but g_r became slightly positive for $R > 4 \times 10^{-10}$ m. In contrast, our present calculations of g_v yielded a pronounced minimum near $R = 3.65 \times 10^{-10}$ m; because information on the variation of g_v with internuclear distance *R* is available for only a few molecular species—specifically, for H_2 [25] and HeH^+ [26] over a large domain and for NaCl [27] over a small domain near R_{e} , we focus attention on this vibrational *g* function in relation to both theoretical calculations and our estimate from spectral data, in our present application of computational spectrometry. Finally one should note that apart from our previous work on LiH [7] several other authors have also analysed the infrared spectra of LiH [28–34].

2. Theory

As the pertinent theory is presented elsewhere [8, 16, 17], we here recall some definitions of important terms. The rotational and vibrational g factors for use with the reduced masses in atomic masses are expressible as a sum of electronic and nuclear contributions,

$$g_{\rm r,v} = g_{\rm r,v}^{\rm el} + g_{\rm r,v}^{\rm nu}$$
 (10)

of which the nuclear contribution for a diatomic molecule is common to both factors and independent of internuclear distance.

$$g_{\rm r,v}^{\rm nu} = m_{\rm p} \frac{Z_a M_b^2 + Z_b M_a^2}{M_a M_b (M_a + M_b)}$$
(11)

The electronic contributions contain sums of transition moments, to electronically excited states of an appropriate symmetry class weighted with the reciprocal of the excitation energies, of the operator for nuclear linear momentum for g_{yy}

$$g_{\rm v}^{\rm el} = -\frac{2m_{\rm p}\hbar^2}{m_{\rm e}\mu} \sum_{n\neq0} \frac{\left|\langle 0|\frac{\partial}{\partial R}|n\rangle\right|^2}{E_{\rm n}(R) - E_0(R)}$$
(12)

which hence involve quantity $-i\hbar\langle 0|\partial/\partial R|n\rangle$ as a nonadiabatic matrix element coupling the electronic ground state $|0\rangle$, having associated wave function $\Psi_0(\{r_i\}; R)$, with electronically excited state $|n\rangle$ of the same symmetry class, with its associated wave function $\Psi_n(\{r_i\}; R)$; formulae relating these sums to coefficients s_j in Eq. (7) are reported elsewhere [16]. Related to magnetic dipolar moment, for angular momentum *L* about the center of mass R_{CM} , with $L_x = L_y$ because of cylindrical symmetry, the corresponding formula for g_r is

$$g_{\rm r}^{\rm el} = -\frac{2m_{\rm p}}{m_{\rm e}\mu R^2} \sum_{n\neq 0} \frac{|\langle 0|L_x(R_{\rm CM})|n\rangle|^2}{E_{\rm n}(R) - E_0(R)}$$
(13)

but here the electronically excited state $|n\rangle$ must have electronic angular momentum Λ differing by

one unit from that of the electronic ground state $|0\rangle$. The relation of this sum to coefficients t_j in Eq. (8) is specified elsewhere [17]. The energies of which differences appear in both latter denominators are electronic energies formally equivalent to potential energy V(R) for nuclear vibration in a particular electronic state, which for the electronic ground state appears in Eq. (3). Because coefficients s_j in Eq. (7) and t_j in Eq. (8) are definable directly [16, 17] at a particular internuclear distance in terms of sums related to the ones in Eqs. (12) and (13), these coefficients are not merely empirical fitting parameters but have a sound theoretical basis.

3. Calculations of Molecular Electronic Structure of LiH

These calculations were performed with a local development version of the program package Dalton [35]. The contributions from sums over states to the rotational and vibrational g factors, to parameters t_i^{Li} , t_i^{H} , s_i^{Li} , and s_i^{H} and to the gradient of electric dipolar moment are efficiently evaluated as linear response functions [36, 37], whereas the electric dipolar moment is a simple expectation value in the electronic ground state, the implementation is described elsewhere [38]. To calculate the rotational g factor, we used rotational London orbitals [39, 40]. We used a multiconfigurational self-consistent-field (MCSCF) wave function [41, 42] with a large complete active space [43], that is, no inactive orbitals and 21 active orbitals in class A_1 , 10 in classes B_1 and B_2 , and four in class A2 of the irreducible representation of point group C_{2v} . This active space is the same as that in our calculation of radial functions for the electric polarizability of LiH [44], but is much larger than in preceding calculations of rotational and vibrational g factors [16, 17, 45]. The one-electron basis set was taken also from the preceding work on the polarizability of LiH [44]; it comprises 13 s-, 8 p-, 6 d-, and 2 f-type sets of uncontracted gaussian functions on Li and 12 s-, 8 p-, and 5 d-type sets of uncontracted gaussians on H; the exponents were taken from a contracted basis set of Roos and Sadlej [46]. The basis set that we used in our previous calculations of rotational [7, 17] and vibrational [16] g factors and of spin-rotation parameters of LiH [47] was based also on the basis set of Roos and Sadlej, but was not totally decontracted, and lacked functions of type f on Li. The results of our calculations of various quantities as a function of internuclear distance appear in Table I. Figure 1 shows points of electronic energy, relative to zero energy at the minimum and expressed as a wavenumber quantity. Our electronic energy, -8.0674 Hartree, at the equilibrium internuclear distance compares well with the "exact" Born–Oppenheimer energy, -8.070549 Hartree, estimated from the experimental binding energy D_e [48]. Figure 2 shows plots of the rotational and vibrational *g* factors, electric dipolar moment |p| and its derivative |dp/dR|, and one nonadiabatic coupling matrix element in Eq. (12) as a function of internuclear distance.

The quality of our calculated radial functions of the rotational g factor $g_r(R)$ and electric dipolar moment p(R) can be judged by comparing the vibrational averages of $g_r(R)$,

$$g_{\mathbf{r}}^{(v,J)} = \left\langle \Theta_{v,J}(R) | g_{\mathbf{r}}(R) | \Theta_{v,J}(R) \right\rangle$$
(14)

and analogously of electric dipolar moment p(R) with the available experimental values [49–51]. The vibration-rotational wavefunctions $\Theta_{v,f}(R)$ were obtained by numerical solution of the nuclear Schrödinger equation

$$\begin{cases} -\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} \right) + \frac{Z_a Z_b e^2}{4\pi \varepsilon_0 R} + V(R) \\ \times \Theta_{v,J}(R) = E_{v,J} \Theta_{v,J}(R) \quad (15) \end{cases}$$

in which, we applied the calculated MCSCF energies as potential energy V(R) for the nuclear motion in this equation. The results of these calculations appear in Table II, in which values of rotational *g* factors pertain specifically to ⁷Li¹H at either the internuclear separation R_e or vibrationally averaged over the vibrational ground state and first excited state, as indicated; the electric dipolar moment *p* in the form of a radial function is independent of isotopic mass for this net electrically neutral molecule.

Our value of the rotational g factor at the separation Re is in perfect agreement with a recent benchmark CCSD(T) result [52] and our dipole moment radial function coincides with an earlier CISD [53] and very recent second order perturbation theory radial function [54]. Furthermore the satisfactory agreement between calculated and measured quantities, with deviations of less than 0.2%, demonstrates the quality of the radial functions for the rotational g factor and electric dipo-

lar moment, and lends confidence to their use as constraints in fitting spectral data. Nevertheless, comparison with experimental values for the vibrational ground state probes mainly our rotational *g*-factor and dipole moment curves in the vicinity of the equilibrium internuclear distance and not near the dissociation limit. We assign, therefore, no physical significance to the deviation of the calculated rotational *g*-factor from zero for internuclear distances larger than 4.0×10^{-10} m, which is certainly due to a decrease in accuracy of our approximated wavefunction for large internuclear distances. These internuclear distances are, however, far outside of the range of internuclear distance relevant for the fitting of spectral data.

4. Analysis of Spectral Data

To convert results in Table I to radial coefficients t_j as coefficients of z^j , we fitted to polynomials the values of $t^{\text{Li}}(R)$ and $t^{\text{H}}(R)$ from these relations,

$$t^{\rm Li}(R) = \mu \left[\frac{g_{\rm r}(R)}{m_{\rm p}} + \frac{2p(R)}{eRM_{\rm H}} \right] \tag{16}$$

$$t^{\rm H}(R) = \mu \left[\frac{g_{\rm r}(R)}{m_{\rm p}} - \frac{2p(R)}{eRM_{\rm Li}} \right]$$
(17)

that enable calculation of the isotopic dependence of the rotational *g* factor as a radial function with polarity $^+AB^- = ^+LiH^-$, as indicated by the calculated values and sign of *p*(*R*) in Table I. These formulae can be derived [17] from Eq. (13) and are consistent with a general partition of the rotational *g* factor into an irreducible contribution and a contribution containing the electric dipolar moment, according to this formula that indicates also the dependence on the masses of separate atoms A and B [8, 17].

$$g_{\rm r}(R) = m_{\rm p}g_{\rm r}^{\rm irr}(R)\left(\frac{1}{M_{\rm a}} + \frac{1}{M_{\rm b}}\right) + \frac{m_{\rm p}}{eR}p(R)\left(\frac{1}{M_{\rm a}} - \frac{1}{M_{\rm b}}\right)$$
(18)

The corresponding formula for the vibrational *g* factor is [8, 16]

$$g_{v}(R) = m_{p}g_{v}^{irr}(R)\left(\frac{1}{M_{a}} + \frac{1}{M_{b}}\right) + \frac{m_{p}dp(R)}{e}\left(\frac{1}{M_{a}} - \frac{1}{M_{b}}\right)$$
(19)

From the tabulated values of $g_r(R)$ and p(R) at each value of *R* in a domain $R/10^{-10}$ m = [1.05,

TABLE I

Electronic energy E_0 , electric dipolar moment p, vibrational g_v , and rotational g_r factors at internuclear distance R for ⁷Li¹H in electronic state X ¹ Σ ⁺.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>R</i> /10 ⁻¹⁰ m	E ₀ /Hartree	<i>p</i> /10 ^{−30} C m	$g_{ m r}$	$g_{ m v}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.05	-7.994350052	-16.44303	-1.8031	0.2486
1.15 -8.025414911 -16.84999 -1.200 0.151 1.25 -8.036600616 -17.08190 -1.2746 0.1092 1.35 -8.052435645 -17.60613 -1.0477 0.0291 1.35 -8.05742373 -17.89172 -0.9584 -0.0044 1.44 -8.0614666611 -18.19025 -0.8147 -0.0657 1.55 -8.066203195 -18.82008 -0.7564 -0.0917 1.55 -8.067175663 -19.14833 -0.7053 -0.1186 1.55 -8.067095170 -19.82565 -0.6247 -0.1366 1.55 -8.067095170 -19.82565 -0.6253 -0.1593 1.7 -8.06509680 -20.17161 -0.5634 -0.1953 1.7 -8.05695260 -21.57140 -0.4070 -0.2260 2.0 -8.055127893 -22.25954 -0.4353 -0.2367 2.1 -8.05127895 -23.54810 -0.3704 -0.297 2.3 -8.039430300 -25.2441780 -0.3704 -0.297 2.4 -8.04867596 -23.54810 -0.3704 -0	1.1	-8.011500191	-16.63474	-1.5936	0.1981
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.15	-8.025414911	-16.84999	-1.4200	0.1510
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.2	-8.036600616	-17.08190	-1.2746	0.1095
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.25	-8.045489390	-17.33524	-1.1520	0.0671
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.3	-8.052435545	-17.60613	-1.0477	0.0297
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.35	-8.057742373	-17.89172	-0.9584	-0.0045
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4	-8.061666611	-18.19025	-0.8814	-0.0361
	1.45	-8.064425535	-18.50019	-0.8147	-0.0651
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.5	-8.066203195	-18.82008	-0.7564	-0.0917
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.55	-8.067155663	-19.14853	-0.7053	-0.1163
1.65 -0.67095170 -19.82565 -0.6205 -0.1593 1.75 -8.06509360 -20.17161 -0.5851 -0.1795 1.8 -8.065033681 -20.52066 -0.5534 -0.1795 1.8 -8.065127893 -22.29545 -0.4760 -0.236 2.0 -8.055127893 -22.29459 -0.4007 -0.2800 2.1 -8.050112404 -22.99459 -0.4007 -0.2800 2.2 -8.044857596 -23.54810 -0.3704 -0.297 2.3 -8.039506202 -24.11859 -0.3433 -0.3376 2.4 -8.034170782 -24.61760 -0.3184 -0.3376 2.4 -8.03842356 -25.32147 -0.2270 -0.4100 2.75 -8.028925412 -25.02839 -0.2949 -0.5673 2.6 -8.023842356 -25.32147 -0.2270 -0.4100 2.75 -8.016613300 -25.49113 -0.2377 -0.5123 3.0 -8.005822077 -24.84864 -0.1793 -0.8573 3.25 -7.99330387 -22.10585 -0.1080 -1.6473 3.3 -7.99330387 -22.10585 -0.1080 -1.6473 3.4 -7.99241383 -20.66748 -0.0854 -1.8688 4.55 -7.998729758 -18.14300 -0.0549 -2.2793 3.6 -7.987647628 -17.25218 -0.00463 -2.2196 3.7 -7.986729799 -15.24241 -0.0310 -2.2046 <td>1.59491123</td> <td>-8.067417267</td> <td>-19.44972</td> <td>-0.6647</td> <td>-0.1366</td>	1.59491123	-8.067417267	-19.44972	-0.6647	-0.1366
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.65	-8.067095170	-19.82565	-0.6205	-0.1592
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.7	-8.066290690	-20.17161	-0.5851	-0.1780
1.8 -8.063543838 -20.87131 -0.5249 -0.2102 1.9 -8.05969260 -21.57140 -0.4760 -0.236 2.0 -8.055127893 -22.25943 -0.4007 -0.2800 2.1 -8.050112404 -22.92459 -0.4007 -0.2800 2.2 -8.044857966 -23.54810 -0.3704 -0.2977 2.3 -8.039506202 -24.11859 -0.3433 -0.3154 2.4 -8.034170782 -24.61760 -0.3184 -0.3377 2.5 -8.023842356 -25.32147 -0.2720 -0.4102 2.75 -8.016613300 -25.49113 -0.2727 -0.5122 3.0 -8.005822077 -24.84864 -0.1793 -0.8573 3.25 -7.998307241 -22.10585 -0.1080 -1.6474 3.3 -7.995310387 -22.10585 -0.1080 -1.6144 3.4 -7.992441383 -20.66748 -0.0854 -1.8688 3.45 -7.99837241 -21.39819 -0.0963 -1.7471 3.4 -7.992441383 -20.66748 -0.0854 -1.8688 3.45 -7.998729758 -18.14300 -0.0549 -2.0799 3.55 -7.98672979 -15.42241 -0.0310 -2.2046 3.75 -7.98672979 -15.42241 -0.0310 -2.2046 3.75 -7.984326631 -11.6372 -0.00463 -2.1997 3.86 -7.98672979 -15.42241 -0.0310 -2.2046 3.75 -7.98672979 <	1.75	-8.065083681	-20.52066	-0.5534	-0.1953
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.8	-8.063543838	-20.87131	-0.5249	-0.2105
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.9	-8.059695260	-21.57140	-0.4760	-0.2364
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.0	-8.055127893	-22.25954	-0.4353	-0.2606
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.1	-8.050112404	-22.92459	-0.4007	-0.2800
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.2	-8.044857596	-23.54810	-0.3704	-0.2974
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.3	-8.039506202	-24.11859	-0.3433	-0.3158
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.4	-8.034170782	-24.61760	-0.3184	-0.3376
2.6 -8.023842356 -25.32147 -0.2720 -0.4102 2.75 -8.016613300 -25.49113 -0.2377 -0.5122 3.0 -8.005822077 -24.8464 -0.1793 -0.857 3.25 -7.996867704 -22.72133 -0.1196 -1.467 3.3 -7.995310387 -22.10585 -0.1080 -1.6144 3.35 -7.993837241 -21.39819 -0.0963 -1.7412 3.4 -7.992441383 -20.66748 -0.0854 -1.8682 3.45 -7.99124757 -19.86620 -0.0749 -1.9826 3.55 -7.989886632 -19.06068 -0.0649 -2.0796 3.55 -7.987647628 -17.25218 -0.0463 -2.199 3.65 -7.986639457 -16.34228 -0.0383 -2.21646 3.7 -7.985702979 -15.42241 -0.0310 -2.2043 3.75 -7.984034441 -13.58851 -0.0188 -2.0986 3.8 -7.98266379 -12.69109 -0.0137 -2.0092 3.9 -7.98296379 -12.69109 -0.0137 -2.0092 3.95 -7.981996211 -10.97070 -0.0056 -1.7840 4.0 -7.979254156 -6.70307 0.00065 -1.6552 4.25 -7.977149024 -2.63273 0.00065 -0.2744 5.0 -7.97671992 -1.63497 0.0048 -0.1402 7.5 -7.97671992 -1.63497 0.00065 -0.2744	2.5	-8.028925412	-25.02839	-0.2949	-0.3673
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.6	-8.023842356	-25.32147	-0.2720	-0.4102
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.75	-8.016613300	-25.49113	-0.2377	-0.5129
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.0	-8.005822077	-24.84864	-0.1793	-0.8573
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.25	-7.996867704	-22.72133	-0.1196	-1.4673
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.3	-7.995310387	-22.10585	-0.1080	-1.6145
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.35	-7.993837241	-21.39819	-0.0963	-1.7412
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.4	-7.992441383	-20.66748	-0.0854	-1.8689
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.45	-7.991124757	-19.88620	-0.0749	-1.9829
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.5	-7.989886632	-19.06068	-0.0649	-2.0798
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.55	-7.988729758	-18.14300	-0.0549	-2.1533
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.6	-7.987647628	-17.25218	-0.0463	-2.1991
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.65	-7.986639457	-16.34228	-0.0383	-2.2164
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.7	-7.985702979	-15.42241	-0.0310	-2.2043
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.75	-7.984835601	-14.50161	-0.0245	-2.1646
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.8	-7.984034441	-13.58851	-0.0188	-2.0987
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.85	-7.983296379	-12.69109	-0.0137	-2.0099
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.9	-7.982618112	-11.81647	-0.0094	-1.9038
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.95	-7.981996211	-10.97070	-0.0056	-1.7840
4.25-7.979254156-6.703070.0060-1.01294.5-7.977915733-4.275050.0075-0.55494.75-7.977149024-2.632730.0065-0.27445.0-7.976671992-1.634970.0048-0.14037.5-7.975938063-0.008190.0000-0.0002	4.0	-7.981427178	-10.15875	-0.0025	-1.6553
4.5-7.977915733-4.275050.0075-0.55484.75-7.977149024-2.632730.0065-0.27445.0-7.976671992-1.634970.0048-0.14037.5-7.975938063-0.008190.0000-0.0002	4.25	-7.979254156	-6.70307	0.0060	-1.0129
4.75-7.977149024-2.632730.0065-0.27445.0-7.976671992-1.634970.0048-0.14037.5-7.975938063-0.008190.0000-0.0002	4.5	-7.977915733	-4.27505	0.0075	-0.5545
5.0 -7.976671992 -1.63497 0.0048 -0.1403 7.5 -7.975938063 -0.00819 0.0000 -0.0002	4.75	-7.977149024	-2.63273	0.0065	-0.2744
7.5 -7.975938063 -0.00819 0.0000 -0.0002	5.0	-7.976671992	-1.63497	0.0048	-0.1403
	7.5	-7.975938063	-0.00819	0.0000	-0.0002
10.0 -7.975935907 -0.00020 0.0000 0.000 ⁻	10.0	-7.975935907	-0.00020	0.0000	0.0001



FIGURE 1. Energy/*hc* of LiH as a function of internuclear separation *R*. The small squares indicate points of electronic energy $E_0(R)$ from calculations of molecular electronic structure relative to zero energy at R_e ; the curve represents potential energy *V*(*R*) from analysis of molecular spectra, and horizontal lines denote energies of vibrational states of ⁷Li¹H with $v = 0 \cdots 6$ in ascending order.

3], we calculated values of $t^{\text{Li}}(R)$ and $t^{\text{H}}(R)$, and then fitted them as a polynomial in *z*, taking sufficient terms to fit the input data essentially within their precision. The resulting values of coefficients t_j^{Li} and t_j^{H} are listed in Table III. An alternative procedure involves fitting of the directly calculated values of $t^{\text{Li},\text{H}}(R)$ [17] to yield essentially the same polynomials.

To achieve a global fit of spectral data of LiH, we applied procedure Radiatom [9]: in the original version (in Fortran) with precision 32 decimal digits, expressions for Y_{kl} [7] were derived symbolically (with program Reduce) through a JBKW treatment [55]; in a new version (entirely in software Maple) with precision 24 decimal digits, all expressions were freshly evaluated symbolically according to hypervirial perturbation theory [56, 57]. We verified that algebraic expressions of term coefficients Y_{kl} derived by either method are identical, but the latter method [56, 57] is computationally more efficient to produce those expressions than the former. Numerical values of parameters derived through Radiatom in either version are not quite identical-because the algorithm for nonlinear regression [9] according to the approach of Levenberg and Marquardt has slightly different implementations, but differences in values are within estimated single standard errors as stated in Table III from the Fortran version. Initial estimates of all unconstrained parameters were set to zero except rough estimates of $U_{1,0}$ and $U_{0,1}$, and generic values of c_1 and c_2 [13]; during progress toward convergence through ~20 iterations, the weighted value of χ^2 decreased from ~10¹³ to ~10³. The duration of a given fit with Maple, for which code is partially interpreted, is about 30 times that with the fully compiled Fortran procedure on computers with comparable speeds of processors. Other fitting of data was affected with Maple procedures.



FIGURE 2. (a) Rotational and vibrational *g* factors, $g_r(R)$ and $g_v(R)$, as a function of internuclear distance, from quantum-chemical calculations; the black curve denotes the result from spectral analysis over its domain of validity, (b) electric dipolar moment p(R) and its gradient dp(R)/dR as a function of internuclear distance *R*, from quantum-chemical calculations, and (c) squared nonadiabatic coupling matrix element $|\langle 0|\partial \partial R|1 \rangle|^2$ connecting electronic ground state $0 = X^{1}\Sigma^{+}$ and electronically excited state $1 = A^{1}\Sigma^{+}$ as a function of internuclear separation *R*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II

Rotational g factor and electric dipolar moment/ 10^{-30} C m of ⁷ Li ¹ H at $R_e = 1.59491123 \times 10^{-10}$ m and for
vibrational states $v = 0$ and 1 and their rotational dependences.

Property		Calculation	Experiment
g _r	R _e	-0.6647	(0 050 (0 · 0 000 (7) ³ · ((0 · 0 0) (0 ⁻⁴ · ((- 1))
	v = 0	$-0.6572 + 1.52 \ 10^{-4} J \ (J+1)$	$(-0.65842 \pm 0.00017)^{a} + (1.2 \pm 0.6) \ 10^{-4} \ J \ (J+1)^{3}$
	<i>v</i> = 1	$-0.6439 + 1.51 \ 10^{-4} \ J \ (J + 1)$	
p	R _e	19.4493	19.439 ^c
	v = 0	19.6376 + 1.25 10 ⁻³ J (J + 1)	$19.620 \pm 0.001^{\circ}$
	<i>v</i> = 1	$20.0004 + 1.29 \ 10^{-3} \ J \ (J + 1)$	$19.982 \pm 0.001^{\circ}$

^aRef. [49].

^b Ref. [50].

^c Ref. [51].

Because our previous analysis of data on LiH [7], new measurements of wave numbers of pure rotational and vibration-rotational transitions of LiH in four isotopic variants—⁶Li¹H, ⁶Li²H, ⁷Li¹H, and ⁷Li²H—were reported [58] up to v = 6 for species involving ⁷Li, ¹H, and ²H, but up to only v = 3 for species involving ⁶Li. We used these data instead of earlier vibration-rotational data of

smaller extent and poorer precision, and combined them with frequency data for pure rotational transitions [59–62] in a global fit of 1000 data that yielded significant values of only 20 adjusted parameters: $c_1 - c_9$, $U_{0,1} = Y_{0,1}/\mu$, $U_{1,0} = Y_{1,0}/\mu^{\frac{1}{2}}$, s_0^{Li} , s_1^{H} , u_1^{Li} , u_2^{Li} , u_1^{H} , u_2^{H} , u_3^{H} , and u_4^{H} , of which the values appear in Table III with a few other derived values. The weight of each

TABLE III

Coefficients of radial functions and associated parameters of LiH X $^{1}\Sigma^{+a}$.				
c ₀ /m ⁻¹	6572379.3 ± 5.6	s ₀ ^{Li}	0.91260 ± 0181	
C ₁	-0.8970678 ± 0.0000057	Ū.		
C ₂	0.348233 ± 0.000040	s ₀ ^H	-0.2612 ± 0.0029	
C ₃	-0.093085 ± 0.000196	s ^H ₁	-0.3733 ± 0.0195	
C ₄	-0.044426 ± 0.00087			
C ₅	0.0765 ± 0.0027	$u_0^{\rm Li}/10^6 {\rm m}^{-1}$	[168.411 ± 0.002]	
C ₆	-0.1143 ± 0.0078	$u_1^{\rm Li}/10^6 {\rm m}^{-1}$	-5.53900 ± 0.0082	
C ₇	-0.2078 ± 0.024	$u_2^{\rm Li}/10^6 {\rm m}^{-1}$	6.357 ± 0.134	
C ₈	0.6024 ± 0.049	$u_0^{\rm H}/10^6~{\rm m}^{-1}$	[12.829 ± 0.002]	
C ₉	-0.7538 ± 0.115	$u_1^{\rm H}/10^6 {\rm m}^{-1}$	-5.15624 ± 0.00096	
$U_{0,1}/{\rm m}^{-1} u$	662.708918 ± 0.000082	$u_2^{\rm H}/10^6~{\rm m}^{-1}$	4.923 ± 0.021	
$U_{1,0}/{\rm m}^{-1} u^{1/2}$	131993.551 ± 0.064	$u_3^{\rm H}/10^6~{\rm m}^{-1}$	-3.340 ± 0.051	
$R_{\rm e}/10^{-10}$ m	1.59491242 ± 0.0000020	$u_4^{\rm H}/10^6~{\rm m}^{-1}$	4.828 ± 0.158	
$k_{\rm e}/{\rm N}~{\rm m}^{-1}$	102.649202 ± 0.000100			
t ₀ ^{Li}	$[0.749508 \pm 0.000142]$	t_{0}^{H}	$[-0.772779 \pm 0.000051]$	
t ₁ ^{Li}	$[0.60714 \pm 0.00115]$	t_1^{H}	[1.28086 ± 0.00047]	
t_2^{Li}	$[-1.2181 \pm 0.0022]$	t_2^{H}	$[-1.7927 \pm 0.00191]$	
t ₃ ^{Li}	[1.077 ± 0.022]	t_3^{H}	$[2.0040 \pm 0.0088]$	
t_4^{Li}	[-1.710 ± 0.106]	t_4^{H}	$[-1.6797 \pm 0.0198]$	
t ₅	[3.546 ± 0.160]	t_{5}^{H}	$[2.375 \pm 0.033]$	
t ₆	$[-2.586 \pm 0.34]$	t_{6}^{H}	$[-0.5685 \pm 0.079]$	
t_{7}^{LI}	$[-6.825 \pm 0.65]$	t_7^{H}	$[-0.8264 \pm 0.042]$	
t_8^{LI}	[6.37 ± 0.31]			

^a In this table, apart from coefficients in radial functions defined through formulae above, appear $U_{1,0}$ and $U_{0,1}$, which correspond to $Y_{1,0}$ and $Y_{0,1}$, respectively, in equation (4) with their dependence on mass eliminated, and equilibrium force coefficient k_e . Values enclosed within brackets are fitted from results of quantum-chemical calculations to serve, except u_0^{\downarrow} and u_0^{H} , as constraints in fits of spectral data. Stated uncertainties represent single standard deviations in the fitting, and uncertainties of k_e and R_e include uncertainties of the pertinent physical constants.

frequency or wavenumber item in the fit was generally a reciprocal of its squared uncertainty. There is considerable scatter of residuals of the pure rotational data [59–62], relative to a standard deviation of a global fit dominated by infrared data [58]; seven data from Matsushima et al. [61] had to be accorded reduced weights. Even so, the reduced standard deviation of the global fit is 1.25, significantly larger than unity, implying that uncertainties assigned to some data by their original authors seem too conservative or that tension remains between measurements of the same transitions in separate laboratories. Further parameters yielded neither statistically significant values nor a significantly improved fit.

5. Discussion

According to the values, in Table III, of $R_{\rm e}$ derived from fitted $U_{0,1}$, of c_0 derived from fitted $U_{1,0}$ and $U_{0,1}$, and of fitted coefficients c_i , $1 \le j \le 9$, and assuming zero values for all further c_i , we evaluated formula (6) for internuclear potential energy V(z) of LiH independent of atomic mass; because the latter experimentally derived quantity from which all mass dependence has been eliminated, which is formally equivalent to electronic energy E_0 from Table I relative to E_0 at R_e , we plot in Figure 1 this curve applicable to the electronic ground state of LiH, X ${}^{1}\Sigma^{+}$, for comparison with our results from quantum-chemical calculations; the vibrational terms for states $0 \le v \le 6$ of ⁷Li¹H are indicated also in Figure 1 to illustrate the range of energy sampled by the included spectral data. The range of energy in which this curve is valid is thus approximately limited by the energy of that state v= 6; the corresponding domain of internuclear distance is $R/10^{-10}$ m = [1.05, 2.47]. In succeeding plots, the region of validity of a formula for a displayed curve in terms of its interval of internuclear distance is indicated approximately by its corresponding projection on the abscissal axes.

We consider next the rotational and vibrational g factors, according to the results of our calculations. Both $g_r(R)$ and $g_v(R)$ are expected to have zero values for internuclear distances R = 0, for the united atom, and $R \rightarrow \infty$, for the separate atoms, and to exhibit at least one extremum between these limits that reflects molecular binding. Comparison of the computed points or the corresponding curves in Figure 2(a) reveals that values of $g_r(R)$ increase monotonically from -1.8

at 1.05×10^{-10} m and appear to approach zero asymptotically as R increases within the domain of calculation, whereas g_v decreases from 0.25 at $R = 1.05 \times 10^{-10}$ m to a pronounced minimum with $g_v = -2.22$ at $R = 3.65 \times 10^{-10}$ m before tending to zero for $R \gg R_{\rm e}$. We observe that our calculated g-factors do not yet approach the united atom limiting values at an internuclear distance 1.05×10^{-10} m. Additional calculations for smaller internuclear distances were computationally impracticable due to convergence problems and linear dependences in the used basis set. Futhermore, these internuclear distances are not relevant for the fitting of available spectral data despite their importance in the study of the limiting behavior of the *g*-factors.

We inquire whether these behaviors might be attributed to either electric dipolar moment p(R)for $g_r(R)$ and its derivative dp(R)/dR for $g_v(R)$, as depicted in Figure 2(c), or the irreducible contributions, $g_r^{irr}(R)$ and $g_v^{irr}(R)$, according to Eqs. (16) and (17), respectively. There is no evident relation between features of curves of p(R) and $g_r(R)$. Figure 3 shows that $g_r^{irr}(R)$ increases from -0.85 at 1.05 \times 10 $^{-10}$ m to a maximum about 0.23 at 3 \times 10^{-10} m and then decreases gradually toward zero with increasing internuclear distance. $g_v^{irr}(R)$ decreases from 0.38 at 1.05×10^{-10} m to a deep minimum, -2.8, at 3.65×10^{-10} m before approaching zero for $R \gg R_e$; that minimum coincides with both the minimum of $g_v(R)$ and the maximum of dp(R)/dR. The latter calculated minimum in $g_v(R)$ lies beyond the domain of internuclear distance to which the available spectral data are sensitive, according to Figure 1. Another interpretation involves recognition of each g factor as



FIGURE 3. Irreducible components, $g_r^{irr}(R)$ and $g_v^{irr}(R)$, of rotational and vibrational *g* functions as a function of internuclear distance, from quantum-chemical calculations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a sum of contributions from the two atomic centers, as indicated in Eqs. (7) and (8) consistent with Eqs. (16) and (17) [8, 16, 17]; explicitly, *g*_v(*R*) becomes the vibrational g factor of a molecule in which $M_{\rm a}$ is infinite so that only atomic center B vibrates, and analogously for $g_r(R)$ [16, 17]. A further interpretation of $g_v^{irr}(R)$ is that this contribution to $g_v(R)$ is inexpressible in terms of expectation values of the wave function for the electronic ground state, unlike the other term involving p(R)[16, 17]. In either case, these two interpretations provide no explanation of a deep minimum of $g_{\rm v}(R)$ at a particular internuclear separation. To discover the source of this minimum, we calculated the nonadiabatic coupling matrix element for transitions between the electronic ground state, denoted X $^{1}\Sigma^{+}$, and the first electronically excited state, A ${}^{1}\Sigma^{+}$, of hence the same symmetry class; the plotted points from this calculation appear in Figure 2(c) for the applicable region. A maximum of the squared nonadiabatic matrix element $\left|\langle 0|\frac{\partial}{\partial R}|1\rangle\right|^2$ that couples electronic ground state X ${}^{1}\Sigma^{+}$ of LiH to electronically excited state A $^1\Sigma^+$ appears at the same internuclear separation 3.65×10^{-10} m. The difference of energies $E_n(R)$ $- E_0(R)$ between electronically excited state A $^{1}\Sigma^{+}$ and electronic ground state $X^{1}\Sigma^{+}$ must be a positive quantity at all internuclear separations because the corresponding curves for potential energy must not intersect. As Eq. (12) indicates, the maximum in the squared matrix element involving the first electronically excited state A ${}^{1}\Sigma^{+}$, hence produces a minimum of $g_{v}(R)$ at R = $3.65~\times~10^{-10}$ m. For H_2, we concluded also that such matrix elements in the numerator of Eq. (12), rather than the energy difference in the corresponding denominator, were responsible for the production of a minimum in that vibrational g factor [25]; in particular, the matrix element coupling the first electronically excited state of class ${}^{1}\Sigma_{g}^{+}$ of H₂ exhibited a maximum near the same internuclear distance at which appeared a minimum of $g_v(R)$, but the exact position of the latter minimum was influenced by the excitation energy and by the coupling to more highly excited states. Likewise for HeH⁺ [26], the extrema in the calculated curve of $g_{v}(R)$ correspond to extrema in the first-order matrix element coupling the electronic ground state and first excited state.

Regarding the adiabatic contributions to the vibration-rotational energies of LiH in its isotopic variants, from values of u_j^{Li} in Table III fitted from spectra plus a constant, u_0^{Li} , derived from

published numerical values at several internuclear distances [1], we derived the following formula to represent a radial function for an adiabatic correction associated with the lithium atomic center independent of atomic mass,

$$\Delta V_{\rm ad}^{\rm Li} / u \, {\rm m}^{-1} = 92385.19 + (-3086.8 \pm 8.2)z + (3597 \pm 73)z^2 \quad (20)$$

which is plotted as a curve in Figure 4(a), with calculated points [1] for comparison; for an additional comparison, an exact polynomial representation of those calculated points [1] yields this formula:

$$\begin{split} \Delta V_{\rm ad}^{\rm Li} / u \,\, {\rm m}^{-1} &= 92385.19 - 3169.90 \,\, z + 4896.87 \,\, z^2 \\ &+ 1987.27 \,\, z^3 - 11905.13 \,\, z^4 - 37933.27 \,\, z^5 \\ &+ 71718.27 \,\, z^6 + 74959.08 \,\, z^7 \quad (21) \end{split}$$

From fitted values of u_j^{H} in Table III, we derive analogously a corresponding formula to represent a radial function for an adiabatic correction associated with the hydrogen atomic center,

$$\Delta V_{\rm ad}^{\rm H}/u \,\,{\rm m}^{-1} = 7035 + (-2828.48 \pm 0.52)z + (2688.2 \pm 11.5)z^2 + (-1405 \pm 59)z^3 + (1331 \pm 187)z^4 (22)$$

which is plotted as a curve in Figure 4(b), with the calculated points [1].

Because data for isotopic species ⁶Li are available to only v = 3 and because the relative mass difference between masses of ⁶Li and ⁷Li is smaller than between ¹H and ²H, the formula for $\Delta V_{ad}^{H}(z)$ in Eq. (9) is truncated at a quadratic term, whereas the quartic polynomial for $\Delta V_{ad}^{Li}(z)$ in Eq. (9) reflects data to v = 6. A corresponding exact fit to calculated points [1] yields

$$\Delta V_{\rm ad}^{\rm H}/u \,\,{\rm m}^{-1} = 7035.2 - 3160.75 \,\,z + 5584.07 \,\,z^2 \\ + \,13854.46 \,\,z^3 - 100067.32 \,\,z^4 \\ + \,13622.76 \,\,z^5 + 502328.20 \,\,z^6 - 523003.44 \,\,z^7 \quad (23)$$

In Figure 4(c), we compare the curve for the total adiabatic correction for ${}^{6}Li^{1}H$ from a sum of corrections of separate atomic centers in Eqs. (20) and (22) divided by their masses,

$$\Delta V_{\rm ad} = \frac{\Delta V_{\rm ad}^{\rm Li}}{M_{\rm Li}} + \frac{\Delta V_{\rm ad}^{\rm H}}{M_{\rm H}} \tag{24}$$



FIGURE 4. (a) Adiabatic correction for atomic center Li as a function of internuclear separation R, (b) adiabatic correction for atomic center H as a function of internuclear separation R, and (c) total adiabatic correction for ⁶Li¹H as a function of internuclear distance R; in all cases, the curve within the domain of its validity is deduced from the spectral analysis with a fixed constant term, and the calculated points arise from theoretical calculations [1].

with the corresponding points for the total calculated adiabatic correction [1]. According to these three plots in Figure 4, the calculated points and curves agree satisfactorily within the appropriate domain; that the values of corresponding coefficients in the Eqs. (20) and (21), or (22) and (23), appear more discordant results in part from the uncertainty in deriving small corrections $\Delta V(R)$ from spectral data prone to error of measurement in the presence of the dominant influence V(R) of wavenumbers and frequencies of spectral transitions, and in part because of the disparate orders of polynomials.

In Figure 5(a), we plot points calculated for $s^{\text{Li}}(R)$ from values of g_v in Table I with a line reflecting the constant term s_0^{Li} in Table III, and in Figure 5(b) the corresponding points for $s^{\text{H}}(R)$ and a curve for $s_0^{\text{Li}} + s_1^{\text{Li}}z$ with values of fitted coefficients in Table III. From those three deduced values of s^{Li} and s^{H} , we generate a formula for the radial dependence of the vibrational *g* factor of ⁷Li¹H,

$$g_{\rm v} = (-0.1291 \pm 0.0039) + (-0.3733 \pm 0.0195)z$$
 (25)

truncated at a linear term because only $s_0^{\text{Li},\text{H}}$ and s_1^{Li} are evaluated significantly with available spectral data; this curve is plotted in Figure 2(a) with calculated points according to Table I. A fit of those calculated data to a polynomial in *z*, in a domain $R/10^{-10}$ m = [1.05, 3.0] that exceeds the domain of internuclear distance sampled in spectral measurements, requires an eighth order for an essentially exact fit,

$$g_{v} = (-0.136553 \pm 0.000056) - (0.69064 \pm 0.00073)z + (0.6381 \pm 0.0038)z^{2} + (0.0435 \pm 0.027)z^{3} - (0.388 \pm 0.056)z^{4} - (0.155 \pm 0.29)z^{5} + (1.402 \pm 0.35)z^{6} - (6.285 \pm 0.93)z^{7} - (17.96 \pm 1.14)z^{8}$$
 (26)

in which the stated uncertainties represent only the standard errors of the coefficients in the fit. The constant terms agree within two larger standard errors, but the coefficient of *z* from spectral data has a magnitude too small despite the correct sign; this disparity reflects in part the lack of s_1^{Li} , in part the much greater order of the polynomial in the latter formula for the calculated data, and in part the experimental error in measurements of transition wavenumbers.

A fit of the data for $g_r(z)$ in Table III requires a polynomial of degree 10 to reproduce all data in a



FIGURE 5. (a) Contribution of atomic center Li to vibrational g factor as a function of internuclear separation R and (b) contribution of atomic center H to vibrational g factor as a function of internuclear separation R; in both cases, small squares denote points from quantum-chemical calculations and the curve is deduced from spectral analysis over the domain of its validity.

domain $R/10^{-10}$ m = [1.05, 3.0] within the precision of the calculation,

$$g_{\rm r} = (-0.664673 \pm 0.000016) + (1.36588 \pm 0.00024)z - (1.9876 \pm 0.0018)z^{2} + (2.1962 \pm 0.014)z^{3} - (1.691 \pm 0.044)z^{4} + (2.876 \pm 0.26)z^{5} - (2.548 \pm 0.38)z^{6} - (5.321 \pm 1.93)z^{7} + (8.273 \pm 1.73)z^{8} + (14.95 \pm 5.0)z^{9} - (21.74 \pm 5.4)z^{10}$$
(27)

in which the stated uncertainties represent only the standard errors of the coefficients in the fit. The full data are plotted in Figure 2(a). Note that g_r is not equal to zero at R_e , as assumed or set for an equivalent quantity by Watson [63].

The curves pertaining to both adiabatic corrections and the vibrational g factor generally conform to points from the quantum-chemical calculations, as a comparison of pertinent formulae also shows. Because the domain of molecular energies sampled in spectral data [58] for isotopic species of LiH containing ⁶Li, up to only v = 3, is less than that for species containing ²H, up to v =6, the corresponding domains of radial functions for atomic center Li are less wide than for H. The slopes and curvatures of curves for both ΔV_{ad}^{Li} and ΔV_{ad}^{H} near R_{e} conform satisfactorily to the plotted points [1], whereas for s^{Li} a lack of detectable slope, indicated by lack of a derivable value of s_1^{Li} , from spectral data is consistent with plotted points, but the experimental magnitude of $s_0^{\text{Li}} =$ 0.9126 in Table III is larger than the value 0.63 calculated at R_e according to Figure 5(a). For coefficients $s^{\rm H}$, the magnitude of $s_0^{\rm H} = -0.261$ and the slope $s_1^{\rm H} = -0.37$ near $R_{\rm e}$ from spectral data are reasonably accurate according to calculated data, but a significant deviation of curvature of the curve in Figure 5(b) should clearly reflect a value of $s_2^{\rm H}$ that is not derivable from the available spectral data. As the value of g_v near R_e is less sensitive to s_0^{Li} than to s_0^{H} , our estimate of $g_{\text{v}} = -0.129$ \pm 0.004 at $R_{\rm e}$ from spectral data is near the calculated value -0.1366; as that estimate was a genuine prediction, made before results of our calculations became available, one might expect that this approach might yield reasonable estimates of the vibrational g factor for molecules for which pertinent calculations have not been made.

The calculated points for both electric dipolar moment p of LiH, for data from Table I and its derivative dp/dR with respect to internuclear separation, plotted together in Figure 2(b), exhibit an extremum of p near $R = 2.75 \times 10^{-10}$ m. A single extremum of dipolar moment is expected for a typical and nominally polar diatomic molecule, because, between a single united atom and the separate atoms as a molecule dissociates in its electronic ground state into neutral atoms, this quantity differs from zero as electronic charge transfers to some extent from one atomic center toward another; the extent of transfer depends on internuclear distance. Instances of such typical behavior are the hydrogen halides [64], whereas CO that exhibits two extrema undergoes a reversal of polarity within a range of internuclear distance near Re [18]. LiH is a strongly polar molecule: the permanent electric dipolar moment of ⁷Li¹H, which is 19.4393 \times 10⁻³⁰ C m at $R_{\rm e}$ fitted from experiment [51], with which our calculation according to Table II agrees satisfactorily, is about three quarters of the value that would apply to a simple cation and anion with charge of magnitude e at that separation. As internuclear distance R increases from R_e for such a strongly polar species, the molecule initially tends toward dissociation into ions—Li⁺ and H⁻, each with one net electronic charge. Because, for all neutral diatomic molecules in their electronic ground states, dissociation into neutral atoms requires less energy than dissociation into ions, at some point for $R > R_e$ the path towards that ionic limit alters instead to the neutral limit for atoms Li and H. In terms of curves for potential energy, one (adiabatic) curve, similar to that depicted in Figure 1, for the electronic ground state with that neutral limit approaches, but fails to cross, another curve for an electronically excited state that correlates with an ionic limit; the point R_x of nearest approach between these curves is called an avoided crossing, which for LiH occurs near 3.5 \times 10^{-10} m [65]. To define adequately various properties in the vicinity of this avoided crossing, we have calculated points for R in small increments, as presented in Table I and appearing in the pertinent plots. Already before a point marking this avoided crossing, the electric dipolar moment of the electronic ground state begins to decay toward zero, but the derivative of dipolar moment with respect to distance has an extremum near this point. The vibrational g factor, which according to Eq. (17) has a contribution from that derivative of dipolar moment, likewise exhibits an extremum near the same point. These features are perceptible in Figures 2(a) and (b). Nonadiabatic vibrational effects, which the electronic contribution to $g_{\rm v}(R)$ reflects, involve squares of matrix elements connecting these same two electronic states of the same symmetry class ${}^{1}\Sigma^{+}$; these matrix elements that produce the values of g_v in Table I have accordingly a large magnitude near R_{x} , as shown in Figure 2(c). In sum, unlike the case of H₂ for which avoided crossings occur between electronically excited states in two separate pairs are not associated with the prominent minimum in the curve of $g_v(R)$, for LiH an avoided crossing involving electronic ground state X ${}^{1}\Sigma^{+}$ and first electronically excited states A ${}^{1}\Sigma^{+}$ is associated with the prominent minimum in the curve of $g_{\rm v}(R)$.

As a result of our combining data from experiment and theoretical calculations [6], we have identified and separated quantitatively the contributions from adiabatic corrections and nonadiabatic rotational and vibrational effects on the energies of molecular vibration-rotational states through auxiliary term coefficients $Z_{kl}^{\text{Li,H}}$ in Eq. (4). As explained in detail elsewhere [13] and mentioned in the introduction above, these term coefficients Z_{kl} can be divided in turn into two components for atoms of each type, Z_{kl}^{v} for purely vibrational effects with an associated centrifugal term, and Z_{kl}^{r} for further rotational effects. These components reflect the fact that, through isotopic variants, one can in principle deduce information about extra-mechanical effects of only two kinds for each atomic type, beyond the function for potential energy derived from purely coefficients Y_{kl} when coefficients Z_{kl} are present to absorb the extra-mechanical effects. Adiabatic corrections contribute only to Z_{kl}^{v} and the rotational g factor only to $Z_{kl}^{\mathbf{r}}$, but vibrational g factor contributes to both [9]. Through separate calculation, one can estimate numerically not only each such contribution but also, and more meaningfully, a ratio of that contribution to the corresponding principal term coefficient Y_{kl} . As that ratio Z_{kl}/Y_{kl} is expected to have a value of order a ratio m_e/M of electronic and atomic mass, further division by the latter ratio might yield values of order unity. In Table IV, we present such values, each with four significant digits, of that ratio $Z_{kl}/Y_{kl}/(m_e)$ M) for k and l of small values for four specified contributions to Z_{kl} and with $M_{\rm H}$ or $M_{\rm Li}$ as appropriate; for this purpose, we use parameters $R_{\rm e}$ and c_j , $0 \le j \le 9$, of potential energy derived from spectra but, in Z_{kl} , parameters s_j , t_j , and u_j of extra-mechanical effects from quantum-chemical calculations, because the latter are more abundant than those from experiment.

As noted above, there is no contribution of g_r through coefficients t_j to purely vibrational term coefficients $Z_{k,0}$; there is likewise no net contribution of g_v through coefficients s_j to rotational term coefficients $Z_{0,l}$ because separate contributions to Z^r and Z^v cancel identically. The fact that there are thus only two contributions to $Z_{0,1}$ in total, with no possible interference from g_v , permit in principle an estimate of g_r and electric dipolar moment p at R_e from spectral data in absence of applied external fields, from spectra of adequate quality and quantity of transitions; such an estimate by this method of g_r of GaH [66] was

TABLE IV

Separate contributions to auxiliary term coefficients Z_{kl} from adiabatic corrections (ad) and vibrational and rotational *g* factors as a ratio with corresponding Y_{kl} divided by a ratio of atomic and electronic masses, so $Z_{kl}/Y_{kl}/(m_e/M)$.

			Li in ⁷ Li ¹ ł	4		
		Z ^r		Z ^v		
k 0	/	<i>g</i> r	g_{v}	ad	g_{v}	
0	2	0.7495	0 6188	-0.0700	0 6188	
0	3	-0.3613	1 852	_1.952	-1.852	
0	4	-2432	3 033	-0.4592	-3.033	
1	0	0	0	-0.3522	0.3095	
1	1	1.124	-0.0697	-2.632	0.4478	
1	2	4.041	0.3809	-11.78	-0.3041	
2	0	0	0	-1.031	0.8135	
2	1	1.888	-0.0362	-56.27	-0.4262	
2	2	-0.5970	-4.144	51.64	5.947	
3	0	0	0	-47.67	-0.3677	
			H in ⁷ Li ¹ F	4		
		Z	r	Z`	1	
k	1	g_{r}	$g_{ m v}$	ad	g_{\vee}	
0	1	-0.7727	0	-0.8764	0	
0	2	-2.827	-0.2255	-2.122	0.2255	
0	3	-7.020	-0.3482	0.7656	0.3482	
0	4	-12.74	-0.1741	18.76	0.1741	
1	0	0	0	-0.2537	-0.1128	
1	1	-0.2714	-0.1087	-6.588	0.2392	
1	2	2.472	-1.033	-90.85	2.113	
2	0	0	0	5.432	-0.0990	
2	1	1.677	-0.4588	179.7	1.854	
2	2	14.20	-3.287	2353	8.934	
3	0	0	0	16.21	0.6157	

subsequently confirmed by quantum-chemical calculations [67]. For LiH, the available spectral data lack sufficient quality and quantity for its isotopic variants for such a purpose. Trends evident from Table IV indicate that, for given k and increasing l, values of this adjusted ratio might have magnitudes much greater than unity, but that magnitudes of contributions from g_v are generally smaller than those from g_r and adiabatic corrections. Whether the latter trend is general remains to be tested with other molecules, but for both H₂ [25] and LiH the magnitudes of g_v at R_e are markedly smaller than of those of g_r there. Although Figure 2(b) demonstrates that values of both g_v and g_r cover comparable ranges, the effect of an avoided crossing might contribute atypically to the magnitude of g_v for $R > R_e$, whereas g_r is unaffected by this particular perturbation from an electronically excited state because of separate symmetry classes. Some magnitudes of the adjusted ratio Z_{kl}/Y_{kl} in Table IV are even comparable with a ratio $M/m_{\rm e}$, which is ~1,837 for ¹H, but the effect on those energies remains small because for corresponding values of k and l the magnitude of Y_{kl} is also much smaller than for $Y_{1,0}$ or $Y_{0,1}$ that are principal contributors to molecular vibration-rotational energies. A common chemical perception of atomic structure within a molecule, as implemented in a traditional separation of electronic and nuclear motions, hence remains a useful approximation, within definable limits. On subtracting the nuclear contribution to the rotational and vibrational g factors form the total values at each internuclear distance, one can calculate the adiabatic and nonadiabatic contributions to coefficients Z_{kl} , and hence, with Eq. (4), these contributions to the energy or spectral term of vibration-rotational state.

Our results here demonstrate that the agreement between radial functions deduced from spectra and resulting from quantum-chemical calculations is satisfactory, within experimental error that is reasonably small for quantities pertaining to, or near, equilibrium internuclear separation $R_{\rm e}$. Through calculation of these radial functions, of which that for V(R) is most critical, one can hence calculate a vibration-rotational spectrum essentially within the error of experimental measurement [6]. This approach is, therefore, a viable alternative to much more complicated calculations of molecular electronic structure undertaken without invocation of separate treatment of electronic and nuclear motions [68]. The latter approach requires a full calculation for each vibration-rotational state and has so far been achieved for states of H₂ with zero total angular momentum of electrons and nuclei [68], thus for only vibrational states, and for LiH [69] in vibrational states v = 0 and v = 1.

6. Conclusions

We present here the first quantum-chemical calculation of the vibrational g factor for a neutral heteroatomic diatomic molecule for internuclear distance over a broad range, with corresponding results for the rotational g factor, the electric dipolar moment and its gradient. Using the latter data as constraints of available spectral data of

frequencies and wave numbers of pure rotational and vibration-rotational transitions of LiH in four isotopic variants, we have estimated the separate contributions of adiabatic corrections and vibrational g factor to the eigenenergies of any heteroatomic diatomic species; our analysis of spectral data is based on a comprehensive molecular Hamiltonian [8] and algebraic expressions for term coefficients Y_{kl} [55, 70] and Z_{kl} [55]. The values of g_v at R_e for LiH from these separate theoretical and experimental approaches agree roughly within error propagated from measurement of frequency data. Previous estimates of $g_{\rm v}$ at Re for several diatomic molecules were implicitly achieved, whenever values of both $s_0^{a,b}$ were significantly evaluated, but such estimates of g_v appear to be more sensitive to the quality and quantity of spectral data available for a given diatomic molecular species than estimates of adiabatic corrections. Intervals in which these radial functions are defined from experimental data are much smaller than the range for which theoretical calculations are practicable, but this condition reflects the quality and quantity of available spectral data. Spectral data of LiH have relative precision $\sim 2 \times 10^{-7}$ or worse, whereas the best available measurements of transitions in the mid infrared region have precision $\sim 2 \times 10^{-10}$ [71]. When measurements approaching the latter precision become more generally available, in data reduction to coefficients of applicable radial functions one must clearly take into account the contributions of $\Delta V_{nad}(R)$ in $\Delta V(R)$ in the effective Hamiltonian, Eq. (3), that we neglect here; apart from that additional term, with its implied dependence on a greater ratio of electronic to atomic masses than we include explicitly, the present approach to analysis of spectral data continues to be applicable. For the present data of LiH, 20 values of fitted coefficients pertaining to specified radial functions and likely about 10 values of constrained parameters, listed in Table III, suffice to reproduce not only at least 1000 measured data almost within their uncertainties but also hundreds of further measured and unmeasured transitions within the same range of vibration-rotational energy. Although only the radial function for the rotational g factor has a truly direct experimental basis, the generally satisfactory agreement between theoretically calculated points and experimentally derived curves for potential energy, adiabatic corrections and the vibrational g factor, within the context of an effective Hamiltonian in Eq. (3), implies that even these artifacts of separation of electronic and nuclear motions can assume almost a physical and chemical significance. The fact that the ratios of magnitudes of the most important term coefficients Z_{kl} for extra-mechanical effects relative to corresponding mechanical coefficients Y_{kl} are of order m_e/M , denoting a ratio of electronic and atomic masses, likewise implies that, to an approximation satisfactory for many chemical purposes, a molecule might be considered to comprise two or more atomic centers, more or less distinct, rather than formally just electrons and atomic nuclei.

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