Dunham's Formalism Applied in Reduction of Spectral Data of Diatomic Molecules and the Development of Computational Spectrometry

J. F. Ogilvie[1] and J. Oddershede[2]

[1]*Escuela de Quimica, Universidad de Costa Rica, San Pedro de Montes de Oca,*
San Jose 2060, Costa Rica
[2]*Syddansk Universitet, Campusvej 55, DK-5230 Odense M, Denmark*

Abstract

We examine the derivation of information about molecular structure and properties from analysis of pure rotational and vibration-rotational spectral data of diatomic molecular species on the basis of Dunham's algebraic formalism, making comparison with results from alternative approaches. According to an implementation of computational spectrometry, wave-mechanical calculations of molecular electronic structure and properties have already played an important role in spectral reduction through interaction of quantum chemistry and spectral analysis.

Contents

1. Introduction 253
2. Basis of analysis to the extent of Dunham's theory 255
3. Basis of analysis beyond Dunham's theory, by van Vleck and others 262
4. Basis of application of Dunham's and van Vleck's theory to analysis of diatomic spectra 269
5. Applications of Dunham's formalism to spectral analysis 274
6. Gallium hydride, GaH 279
7. Dihydrogen, H_2 288
8. Lithium hydride, LiH 291
9. Carbon oxide, CO 297
10. Discussion 304
11. Conclusion 312
Acknowledgements 313
References 314

1. INTRODUCTION

During the brief span 1904–1933 of his life, James Lawrence Dunham published only five technical papers [1–5], but they continue to exert a significant impact on approaches to analysis of spectra of diatomic molecules. For instance, in 1950

ADVANCES IN QUANTUM CHEMISTRY, VOLUME 48
ISSN: 0065-3276 DOI: 10.1016/S0065-3276(05)48016-8

Herzberg cited Dunham's work at more than eight points in his monograph [6] on spectra of diatomic molecules; of at least 1940 total citations of those five papers, about 29 appeared during year 2003 [7], and in other papers of unknown number published each year authors allude to Dunham's work through his name without citing his publications. Because Dunham's work might in recent years be more frequently cited than its significance be understood, the centennial anniversary of his birth seems a fitting occasion to review why his work maintains a strong influence on this narrow but both pedagogically and practically momentous sector of optical spectroscopy: this field of spectra of diatomic molecules is important pedagogically because their properties illustrate fundamental principles of quantum effects typically explained in terms of an oscillator in one dimension, and practically because many diatomic molecules that are crucial to a comprehensive treatment of atmospheric chemical phenomena are detected through their spectra in absorption, emission or Raman scattering; in either case Dunham's formalism is not merely applicable but prominent. After the discovery of deuterium through observation of a visible spectral line [8] that intensified investigation of isotopic effects, in 1936 van Vleck [9] extended Dunham's formalism to encompass deficiencies that Dunham partly recognised [5], and their collective results and subsequent extension enable a quantitative description of essentially all effects of nuclear mass in band spectra, requiring in addition only effects of nuclear volume to complete treatment of frequency data and effects of vibration-rotational interaction for intensity data. Over the ensuing decades other workers have contributed to details of this treatment through their experimental and theoretical analyses, making an approach to spectral analysis based on this formalism comprehensive and thoroughly practicable. Our present task is to assess this approach, from both experimental and theoretical points of view, in the light of the current status of spectral measurements on diatomic molecules.

For the first time in application to details of spectral analysis, we recognise also the role of wave-mechanical computations that herald the emergence of computational spectrometry as a partner with experimental and theoretical spectrometry in revealing information about molecular structure and properties: in relating frequencies and strengths of spectral lines to molecular properties, the work of Dunham and of van Vleck, for instance, constitutes theoretical spectrometry, whereas the measurement of those frequencies and strengths, with concomitant assignment to transitions between quantum states and fitting of spectral data to theoretical quantities, is the practice of experimental spectrometry. The concern of computational spectrometry is a quantum-chemical calculation, through methods applicable to molecular electronic structure, of some or all factors that affect the frequency and strength of a spectral line with an accuracy comparable with that of typical contemporary research measurements. As a consequence of subsequent evolution, the effective hamiltonian underpinning the results of Dunham and van Vleck is directly appropriate for the practice of computational spectrometry.

In an analysis of a molecular spectrum, the primary task is, for purpose of characterisation, to assign each narrow spectral feature to a transition between two molecular states specified with rotational, vibrational and electronic quantum numbers or other indices. Nearly as important as the former, another task is to represent archetypal properties of each spectral line – the frequency at maximum intensity and its total intensity – by means of formulae that reproduce those features, within the accuracy of their measurement, with parameters fewer than the number of features represented. The latter process constitutes data reduction; apart from compactness in relation to storage and retrieval of data, an advantage of such a reduced representation in an appropriately selected form is a possibility of modest extrapolation of data so as to allow prediction of further features beyond a range of measurements included in reduced data. Even though gross extrapolation, in absence of both exact data and an exact theoretical model, be a practice statistically unreliable and hence universally deprecated, a limited extent serves as a legitimate basis for tentative further investigation and for verification of the correctness of a theoretical formulation. For atomic spectra a seminal instance of such data reduction was Balmer's success in reproducing, within the accuracy of their measurement, the wave lengths of four lines emitted by atomic H by means of a formula containing only one parameter and one integer variable [10]; subsequent discovery of lines in other series led to modification of that formula so as to apply to all series with only two integer variables. In this particular case, the parameter – actually, or proportional to, the Rydberg constant – has direct physical significance in relation to the energy of ionisation of a hydrogen atom. For molecular spectra an observation of Deslandres, almost concurrent with Balmer's discovery, that the separation of wave numbers of many lines in a band system of CN in emission increases nearly linearly [11] enabled fitting of a formula containing only three parameters [6, p. 42]. In this case, and typically for subsequent analyses of infrared and Raman spectral data pertaining to gaseous diatomic samples, parameters are merely artefacts of a particular formulation or model, inaccessible to direct physical measurement. This distinction concerning the observable nature of parameters is important in subsequent discussion.

2. BASIS OF ANALYSIS TO THE EXTENT OF DUNHAM'S THEORY

Although Dunham's first three papers [1, Intensities in the harmonic band of hydrogen chloride; 2, Intensities of vibration-rotation bands with special reference to those of HCl; 3, The isotope effect on band spectrum intensities] treated spectral intensities, two most commonly cited papers [4, The Wentzel-Brillouin-Kramers method of solving the wave equation; 5, The energy levels of a rotating vibrator] pertain to energies of molecular states in relation to frequencies of spectral lines observable such as through measurements of infrared absorption and emission or Raman scattering by diatomic molecular substances in gaseous samples at small total densities; band spectra involving also transitions between electronic states might be another source of such data. As the inverse of wave length, wave number $\tilde{\nu}$ is proportional to frequency, but was measurable more precisely than the knowledge of the speed c of light in vacuo, before the value of that fundamental constant became eventually fixed. We work strictly with wave number of a narrow spectral line of a particular isotopic species as a difference between values of spectral terms [6] of combining states according to Bohr's relation:

$$\tilde{\nu} = E^{i}_{v'J'} - E^{i}_{v''J''} \tag{1}$$

here a term value $E^{\mathrm{i}}_{\mathrm{v'J'}}$, pertaining to a state of discrete energy characterised with quantum numbers principally vibrational v' and rotational J' (and others), implies greater energy than another term value $E^{\mathrm{i}}_{\mathrm{v''J''}}$ specified with quantum numbers v'' and J'' that take generally integer values, for these two states that combine in a transition $|v', J'\rangle \leftarrow |v'', J''\rangle$ in absorption, in accordance with standard practice [6]. Before Dunham's last publication, these term values pertaining to the same electronic state and to a particular isotopic species i were commonly represented implicitly or explicitly through a double sum involving vibrational v and rotational J quantum numbers in functionals to various powers in a form

$$E^{\mathrm{i}}_{\mathrm{vJ}} = \sum_{k=0}\sum_{l=0} A^{\mathrm{i}}_{\mathrm{kl}}(v + 1/2)^{k}[J(J + 1)]^{l} \tag{2}$$

in which term coefficients $A^{\mathrm{i}}_{\mathrm{kl}}$ are regarded as merely *phenomenological fitting parameters* [12], freely adjustable, of arbitrarily selectable subscripts and of minimal number, to obtain an optimal fit according to a selected criterion, such as a minimum sum of squares of residuals; $A_{0,0} = 0$ for the electronic ground state. Earlier usages of just v as a simple integer variable pertaining to a vibrational motion and of $J + ½$ as a functional pertaining to rotational motion were superseded when quantum mechanics became applied to spectra through analogies to a simple linear harmonic oscillator and a rigid rotor [6]; as no real molecule is a rigid rotor – nor an harmonic oscillator – in its nuclear motions within an electronic framework, there is no logical basis to prefer $J\,(J + 1)$ to $(J + ½)^2$, for which the differences $(¼)^l\ A^{\mathrm{i}}_{\mathrm{kl}}$ are readily accommodated, but the former convention is tenaciously established. In such implicit usage for a particular isotopic variant, term coefficients were generally denoted unsystematically such as in the following correspondences, some of which involve compound symbols,

$$\begin{aligned} A_{1,0} &= \omega_{\mathrm{e}}, & A_{2,0} &= -\omega_{\mathrm{e}}x_{\mathrm{e}}, & A_{3,0} &= \omega_{\mathrm{e}}y_{\mathrm{e}}, \\ A_{0,1} &= B_{\mathrm{e}}, & A_{1,1} &= -\alpha_{\mathrm{e}}, & A_{2,1} &= \gamma_{\mathrm{e}}, \\ A_{0,2} &= -D_{\mathrm{e}}, & A_{1,2} &= -\beta_{\mathrm{e}}, & A_{0,3} &= H_{\mathrm{e}}, \end{aligned} \tag{3}$$

in values of rotational terms for a particular vibrational state,

$$\mathrm{F}_{\mathrm{v}}(J) = B_{\mathrm{v}}[J(J + 1)] - D_{\mathrm{v}}[J(J + 1)]^2 + H_{\mathrm{v}}[J(J + 1)]^3 + \ldots \tag{4}$$

and of vibrational terms,

$$\mathrm{G}(v) = \omega_{\mathrm{e}}(v + 1/2) - \omega_{\mathrm{e}}x_{\mathrm{e}}(v + 1/2)^2 + \omega_{\mathrm{e}}y_{\mathrm{e}}(v + 1/2)^3 + \ldots \tag{5}$$

with subsidiary relations,

$$B_{\mathrm{v}} = B_{\mathrm{e}} - \alpha_{\mathrm{e}}(v + 1/2) + \gamma_{\mathrm{e}}(v + 1/2)^2 + \ldots \tag{6}$$

$$D_{\mathrm{v}} = D_{\mathrm{e}} + \beta_{\mathrm{e}}(v + 1/2) + \ldots \tag{7}$$

and so forth, with some variability, depending on researcher, of inclusion ad hoc of minus signs to make selected parameters assume generally positive values. In an absence of net orbital, electronic and nuclear spin momenta that might couple with rotational angular momenta, a sum of these vibrational and rotational terms is simply the value of a spectral term, $E^{\mathrm{i}}_{\mathrm{vJ}} = \mathrm{G}(v) + \mathrm{F}_{\mathrm{v}}(J)$, within a particular electronic state. The objective of fitting wave numbers of spectral lines in perceived sets to expressions involving quantum numbers v and J is to enable reproduction of those wave numbers of many lines with fewer parameters within formulae of simple form. Sufficient parameters of selected kind are employed to reproduce data satisfactorily. By means of coefficients either $A^{\mathrm{i}}_{\mathrm{kl}}$ or their unsystematic equivalents, spectral reduction might be generally achieved such that these parameters number only about one quarter of the number of wave numbers of measured transitions.

In his last paper Dunham obtained a formula for values of spectral terms for a particular isotopic species i in a particular electronic state, which we suppose generally to be of symmetry class $^1\Sigma$ or 0 implying neither net electronic orbital nor net intrinsic electronic angular momentum;

$$E^{\mathrm{i}}_{\mathrm{vJ}} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} Y^{\mathrm{i}}_{\mathrm{kl}}(v + 1/2)^k[J(J + 1)]^l \tag{8}$$

we likewise ignore intrinsic angular momenta of atomic nuclei. This expression appears similar to formula 2, but here $Y_{0,0} \neq 0$, even for an electronic ground state. Dunham actually wrote K instead of J with no explanation of that symbol, but during that era such a symbol to denote rotational angular momentum was common practice. Correspondences with unsystematic parameters are only approximate:

$$\begin{aligned} &Y_{1,0} \cong \omega_{\mathrm{e}}, \quad &&Y_{2,0} \cong -\omega_{\mathrm{e}}x_{\mathrm{e}}, \quad &&Y_{3,0} \cong \omega_{\mathrm{e}}y_{\mathrm{e}},\\ &Y_{0,1} \cong B_{\mathrm{e}}, &&Y_{1,1} \cong -\alpha_{\mathrm{e}}, &&Y_{2,1} \cong \gamma_{\mathrm{e}},\\ &Y_{0,2} \cong -D_{\mathrm{e}}, &&Y_{1,2} \cong -\beta_{\mathrm{e}}, &&Y_{0,3} \cong H_{\mathrm{e}}, \end{aligned} \tag{9}$$

An important distinction between term coefficients $A^{\mathrm{i}}_{\mathrm{kl}}$ and $Y^{\mathrm{i}}_{\mathrm{kl}}$ is that, whereas the former are regarded as freely adjustable, the latter are formally inter-related; for instance, although a relation

$$Y_{0,2} \approx -4Y^3_{0,1}/Y^2_{1,0} \tag{10}$$

thus connecting D_{e}, B_{e} and ω_{e}, might be derivable directly from perturbation theory, other relations such as

$$Y_{0,3} \approx 8Y^3_{0,1}(Y_{1,1}Y_{1,0} + 12Y^2_{0,1})/(3Y^4_{1,0}) \tag{11}$$

thus connecting H_{e}, α_{e}, B_{e} and ω_{e}, are less readily derived without an intermediate model. It is essentially a truism to state that the essence of Dunham's approach to analysis of molecular spectra involves the *primacy of Dunham coefficients* Y_{kl}, that differ from freely adjustable coefficients A_{kl} in being explicitly related to each other through algebraic formulae, such as that above, although many authors of papers involving reduction of spectral data have ignored this distinction.

Two further comments about formula 8 and its parameters are noteworthy. The number of terms with coefficients $Y^{\mathrm{i}}_{\mathrm{kl}}$ in the double sum is formally doubly infinite so that formula 8 can represent spectral terms involving arbitrarily large values of v and J; with data of finite extent the sums become truncated in a systematic and consistent manner conforming to parameters of a minimum number required according to that intermediate model. Instead of exact equalities in formulae 10 and 11, the approximations arise because each term coefficient $Y^{\mathrm{i}}_{\mathrm{kl}}$ constitutes a sum of contributions [5],

$$Y^{\mathrm{i}}_{\mathrm{kl}} = \sum_{m=0} Y^{2\mathrm{m}}_{\mathrm{kl}} \tag{12}$$

of which magnitudes of successive contributions $Y^{(0)}_{\mathrm{kl}}, Y^{(2)}_{\mathrm{kl}}, Y^{(4)}_{\mathrm{kl}}$... for a particular isotopic species generally decrease rapidly with increasing value of m, hence assuring rapid convergence for not too large values of v and – particularly – J; a superscript, $2m$ with m integer, denoting order of contribution takes only even values by dint of their relation to a JBKW procedure [13], based on that developed concurrently by Brillouin [14,15], Kramers [16] and Wentzel [17], itself dependent on a mathematical method developed by Jeffreys [18], according to which Dunham originally derived expressions for these term coefficients [4]. The approximate relations 10 and 11 become exact equalities when only leading contributions $Y^{(0)}_{\mathrm{kl}}$ are employed in those, and analogous, relations. The effect of atomic mass varies for these contributions; denoting by U_{kl} a factor independent of mass in $Y^{(0)}_{\mathrm{kl}}$, we express this dependence on reduced mass μ of a particular isotopic species as

$$Y^{(0)}_{\mathrm{kl}} \propto \mu^{-(\mathrm{k}+2\mathrm{l})/2}, \quad Y^{(0)}_{\mathrm{kl}} = U_{\mathrm{kl}}\mu^{-(\mathrm{k}+2\mathrm{l})/2} \tag{13}$$

in which the molecular reduced mass is defined as $\mu = M_{\mathrm{a}}\, M_{\mathrm{b}}/(M_{\mathrm{a}} + M_{\mathrm{b}})$, with M_{a} and M_{b} being masses of separate neutral atoms into which a diatomic molecule AB, whether net electrically neutral or a molecular ion, dissociates. For further contributions $Y^{(2)}_{\mathrm{kl}}, Y^{(4)}_{\mathrm{kl}}$..., the corresponding factors incorporating reduced mass are respectively $\mu^{-(\mathrm{k}+2\mathrm{l}+2)/2}, \mu^{-(\mathrm{k}+2\mathrm{l}+4)/2}\ldots$

Dunham achieved inter-relations between term coefficients $Y^{\mathrm{i}}_{\mathrm{kl}}$ through use of an intermediate radial function V(R) in an effective hamiltonian for motion of atomic nuclei of this form,

$$\mathcal{H}(R) = \hat{p}^2/(2\mu) + \hbar^2 J(J+1)/(2\mu R^2) + \mathrm{V}(R) \tag{14}$$

that contains terms to represent kinetic energy parallel and perpendicular to an internuclear vector with the centre of mass as origin of coordinates, and potential energy V(R), respectively; the second term hence corresponds to rotational motion about the centre of mass. Here $\hat{p}$ is a linear momentum conjugate to a vector to represent instantaneous internuclear separation R, and the next term involves the square of an angular momentum that takes discrete values $\hbar[J(J+1)]^{1/2}$, with J a non-negative integer or half integer. Instead of direct use of this variable R, Dunham employed a reduced displacement x, thus dimensionless,

$$x = (R - R_\mathrm{e})/R_\mathrm{e}, \quad R = R_\mathrm{e}(1+x) \tag{15}$$

in which R_e denotes an equilibrium internuclear distance, for a particular electronic state, at which the postulated internuclear potential energy $\mathrm{V}(R)$ or $\mathrm{V}(x)$ associated with nuclear motion along the internuclear vector is a minimum; $x=0$ at $R=R_\mathrm{e}$. To avoid working with coefficients of which the units vary with the power of that variable, such a dimensionless variable is highly desirable. According to a formal separation of electronic and nuclear motions, the total electronic energy plus the coulombic repulsion between stationary nuclei becomes a potential energy for motion of those nuclei. Dunham actually employed, instead of x, a greek letter ξ, but in much subsequent work [13] the former symbol is adopted, as here; apart from ease of typewriting, relation to further symbols y and z for cognate variables is facilitated. Dunham adopted a function of potential energy having the form of a polynomial or truncated power series,

$$\mathrm{V}(x) = V_0 + hca_0x^2\left(1 + \sum_{j=1} a_\mathrm{j}x^\mathrm{j}\right) \tag{16}$$

in which V_0 is the potential energy at the minimum; for the electronic ground state of a particular molecular species with a particular net electric charge $V_0 \equiv 0$, and the polynomial is truncated as limited by an extent of available spectral data. The leading term $a_0\, x^2$ of this radial function, which remains if all $a_j=0$ for $j>0$, corresponds to potential energy of the canonical linear harmonic oscillator, for which classically the frequency is independent of vibrational amplitude and quantally the frequency of transitions between adjacent terms is constant; further terms $a_\mathrm{j}\, x^\mathrm{j}$ that make an oscillator anharmonic hence take into account how transitions of a real molecule differ from a limiting harmonic behaviour near $R = R_\mathrm{e}$. In terms of these coefficients for potential energy, term coefficients such as

$$Y_{1,1}^{(0)} = 6B_\mathrm{e}^2(1+a_1)/\omega_\mathrm{e} \tag{17}$$

and

$$Y_{0,3}^{(0)} = 16B_\mathrm{e}^5(3+a_1)/\omega_\mathrm{e}^4 \tag{18}$$

thus become simply related to each other, as here through formula 11 for instance, on elimination of coefficients a_j for potential energy.

Dunham [5] derived these expressions $Y_\mathrm{kl}^\mathrm{i}(\omega_\mathrm{e}, B_\mathrm{e}, a_\mathrm{j})$, necessarily manually, through a JBKW procedure, which he claimed to make more general [4] than what had appeared in previous literature. Dunham reported expressions Y_kl^i containing coefficients a_j up to a_6, and Sandeman [19] and Woolley [20] extended manually these results according to a roughly analogous procedure. Kilpatrick [21] applied perturbation theory in successive orders to derive expressions for Y_kl^i, and Bouanich [22] applied Rayleigh-Ritz perturbation theory for solution of

Schrodinger's equation with a separate Fortran programme to calculate each numerical coefficient of a term in $Y^{\mathrm{i}}_{\mathrm{kl}}$ comprising products of various a_{j}; Brukhanov and coworkers [23] also employed perturbation theory but produced with computer algebra many expressions for $Y^{\mathrm{i}}_{\mathrm{kl}}$. Bessis and coworkers conducted calculations of $Y^{\mathrm{i}}_{\mathrm{kl}}$ of a complicated symbolic nature according to a method involving differential operators [24], at first manually, but invoked computer algebra to assist extension of this approach [25]. The JBKW method has been programmed, with an algorithm [26] similar to Dunham's, or more directly [27]. Uehara has reported explicit expressions for a few coefficients [28,29], also derived with this JBKW method and with symbolic computation. The most efficient algorithm to generate extensive expressions of Y_{kl} is based on hypervirial perturbation theory, or perturbation theory without wave functions [30]. Both matrix mechanics with perturbation theory [31] and classical mechanics [32,33,13] have been applied to the effective hamiltonian in formula 13 to yield expressions for term coefficients $Y^{\mathrm{i}}_{\mathrm{kl}}$. With unequally spaced Fourier components [33,13], according to even classical mechanics one would produce expressions for these term coefficients identical with those from all other approaches listed above.

Before 1977 many spectroscopists reduced their wave number data to phenomenological term coefficients $A^{\mathrm{i}}_{\mathrm{kl}}$ for a particular isotopic species; despite imposing no inter-relations of types in expressions 10 and 11, they employed notation $Y^{\mathrm{i}}_{\mathrm{kl}}$, thus failing to recognise the profound significance of Dunham's work. This approach involves only linear regression, with readily obtainable uncertainties associated with those parameters $A^{\mathrm{i}}_{\mathrm{kl}}$, but many coefficients of correlation between those parameters inevitably assume magnitudes near unity. In other cases some workers selected a subset of these term coefficients, typically $Y_{\mathrm{k,0}}$ and $Y_{\mathrm{k,1}}$ taking as many values of k in each as required, from which to evaluate a few coefficients a_{j} for potential energy; non-linear fitting is required, best performed iteratively until convergence to self consistency. In 1978 the distinction between freely fitted coefficients $A^{\mathrm{i}}_{\mathrm{kl}}$ and coefficients $Y^{\mathrm{i}}_{\mathrm{kl}}$ was formally recognised [12]. Only in 1976 was undertaken [34] the first analysis of error associated with these parameters a_{j}. With spectral data comprising wave numbers of only moderate precision, discrepancies between freely fitted coefficients $A^{\mathrm{i}}_{\mathrm{kl}}$ and coefficients $Y^{\mathrm{i}}_{\mathrm{kl}}$ calculated from parameters for potential energy are generally not much greater than experimental error of evaluation of those quantities $A^{\mathrm{i}}_{\mathrm{kl}}$. In 1974 there had already been noticed significant discrepancies of this nature for CO in precise spectral measurements of multiple isotopic variants [35]; further empirical term coefficients $\Delta^{\mathrm{a,b}}_{\mathrm{kl}}$ associated with separate atomic centres A or B in diatomic molecular species AB were hence introduced and evaluated significantly. According to this formula proposed empirically,

$$E^{\mathrm{i}}_{\mathrm{vJ}} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} U_{\mathrm{kl}}\mu^{-(\mathrm{k}+2\mathrm{l})/2}[1 + m_{\mathrm{e}}(\Delta^{\mathrm{a}}_{\mathrm{kl}}/M_{\mathrm{a}} + \Delta^{\mathrm{b}}_{\mathrm{kl}}/M_{\mathrm{b}})](v + 1/2)^{k}[J(J+1)]^{l} \quad (19)$$

parameters $\Delta^{\mathrm{a,b}}_{\mathrm{kl}}$, like U_{kl} defined in formula 13, are formally independent of atomic mass within sets of isotopes of atoms A or B; for an electronic ground state there exist neither $U_{0,0}$ nor $\Delta_{0,0}^{\mathrm{a,b}}$. The latter parameters $\Delta_{\mathrm{kl}}^{\mathrm{a,b}}$ tend to accumulate a contribution from $Y_{\mathrm{kl}}^{(2)}$ in formula 12. For parameters U_{kl} not interrelated through formulae similar to 11, thus lacking a defined relation to Dunham coefficients Y_{kl} according to formula 13 and becoming merely further phenomenological fitting parameters, analogous to A_{kl} but still independent of isotopic mass, we propose a distinguishing symbol B_{kl}.

Notwithstanding these developments, some spectroscopists continued to express their results in terms of only freely fitted coefficients $A_{\mathrm{kl}}^{\mathrm{i}}$, and obtained from an arbitrarily selected subset thereof divergent values of coefficients a_{j} for the same molecular species in isotopic variants. For HCl [36], derived values of a_6 in formula 16 for $^1H^{35}Cl$ and for $^1H^{37}Cl$ differed by ten times the stated standard errors of these quantities, but these disparate results proved no cause for concern because they reproduced successfully the wave numbers of transitions of each isotopic species through their insertion into expressions for coefficients $Y_{\mathrm{kl}}^{\mathrm{i}}$. For $^1H^{81}Br$, fitting spectral data directly to term coefficients $A_{\mathrm{kl}}^{\mathrm{i}}$ in a linear fit resulted in a reduced standard deviation $\hat{\sigma}=0.76$, indicating by its magnitude less than unity that estimates of uncertainties of measurements of wave numbers of spectral lines were somewhat conservative, whereas fitting the same spectral data directly to coefficients a_{j} through expressions for $Y_{\mathrm{kl}}^{\mathrm{i}}$ resulted in a reduced standard deviation $\hat{\sigma}=1.3$ [37]; that these values of $\hat{\sigma}$ appear to differ significantly might reflect the effect of "*l*-uncoupling" phenomena to which Dunham alluded [5], or other factors not taken into account [37].

Apart from the distance variable x that Dunham used in his function $\mathrm{V}(x)$ for potential energy, other variables are amenable to production of term coefficients $Y_{\mathrm{kl}}^{\mathrm{i}}$ in symbolic form as functions of the corresponding coefficients in a power series of exactly the same form as in formula 16. Through any method to derive algebraic expressions for Dunham coefficients $Y_{\mathrm{kl}}^{\mathrm{i}}$, the hamiltonian might have x as its distance variable, but after those expressions are produced they are convertible to contain coefficients of other variables possessing more convenient properties. To replace x, two defined variables are y [38],

$$y = (R - R_{\mathrm{e}})/R, \quad R = R_{\mathrm{e}}/(1 - y) \tag{20}$$

for which the leading term $\mathrm{V}(y)=b_0\, y^2$ in an expansion for potential energy was the first function for interatomic potential energy, devised by Kratzer [39], and for which Fues made a subsequent wave-mechanical treatment [40], and z [41]:

$$z = 2(R - R_{\mathrm{e}})/(R + R_{\mathrm{e}}), \quad R = R_{\mathrm{e}}(2 + z)/(2 - z) \tag{21}$$

The latter variable eliminates a finite range [42] of convergence of series both of x at $2\, R_{\mathrm{e}}$, because of a pole due to internuclear coulombic repulsion as $R \to 0$, and of y at $\frac{1}{2}\, R_{\mathrm{e}}$, for a similar phenomenon as $R \to \infty$. Expressions for $Y_{\mathrm{kl}}^{\mathrm{i}}$ in terms of coefficients c_{j} in the latter series are available in a large consistent collection in Fortran coding [43] up to c_{10}; such expressions, readily calculated, through symbolic computation with efficient procedures [44], first in terms of coefficients a_{j} and thence converted to b_{j} or c_{j} as required, are further converted to Fortran or C code for numerical applications.

3. BASIS OF ANALYSIS BEYOND DUNHAM'S THEORY, BY VAN VLECK AND OTHERS

Dunham recognised that his theory was adequate only when motions of electrons are totally correlated to one or other nucleus during molecular vibration and rotation about the centre of mass, to which motions Dunham referred as mechanical effects [5]; especially with highly precise measurements of wave numbers of transitions through a large spectral range or range of vibrational quantum numbers, such an assumption is evidently untenable. The principal reason that Dunham's theory is inadequate is that the hamiltonian for nuclear motion lacks terms to take into account the true nature of a diatomic molecule – that it contains not two structureless atoms but two atomic nuclei, each of finite mass and size, and their associated electrons, and that these electrons fail to follow perfectly one or other nucleus in its rotational and vibrational motions with respect to the centre of molecular mass; in the light of Dunham's term, we describe these effects as extra-mechanical [13]. Considering nuclear mass subsequently, we devote attention first to effects of nuclear size.

A hamiltonian commonly applied to describe the electronic structure of a molecule includes a coulombic or electrostatic term arising from a point-like centre of charge for each nucleus. As is generally known by chemists but with implications still largely ignored, an atomic nucleus has extension in space, with a root-mean-square radius of order typically 2×10^{-15} m: the distribution of electronic charge and the electronic energy are accordingly perturbed by this extended distribution of nuclear charge, resulting in slight shifts of energy relative to an hypothetical unperturbed coulombic potential [45]. These shifts of energy lack direct spectral observation, but variations in shifts occur on isotopic substitution because the spatial distribution of nuclear charge varies from one nuclidic species of a particular chemical element to another. Discussing in 1922 an influence of nuclear volume on atomic spectra, Bohr [46] suggested that spectral shifts reflected a variation of internal nuclear structure between isotopic nuclei, producing a correspondingly varying field of force surrounding those nuclei [47]. Not only variation of nuclear volume but also variation of nuclear shape or of a distribution of nuclear charge produces a field shift [48]. Despite the latter complication, discussion of a field shift in regard to molecular spectra is couched conventionally in terms of mean squared nuclear radius $\langle r^2\rangle_{\mathrm{a,b}}$ of atomic centre A or B, by means of an extended relation

$$Y_{\mathrm{kl}}^{(0)} + Z_{\mathrm{kl}}^{\mathrm{f,a}} + Z_{\mathrm{kl}}^{\mathrm{f,b}} = U_{\mathrm{kl}}\mu^{-(2\mathrm{k}+1)/2}(1 + V_{\mathrm{kl}}^{\mathrm{a}}\langle r^2\rangle_{\mathrm{a}} + V_{\mathrm{kl}}^{\mathrm{b}}\langle r^2\rangle_{\mathrm{b}}) \tag{22}$$

with term coefficients U_{kl} independent of mass and volume as defined in formula 13, and $Z_{\mathrm{kl}}^{\mathrm{f}}$ collecting additional terms containing mean squared nuclear radii separately for both atomic centres A and B. Parameters $V_{\mathrm{kl}}^{\mathrm{a,b}}$ for the field shift are functions of electronic density $\rho_{\mathrm{el}}^{\mathrm{a,b}}(R)$ that varies with internuclear distance. Here follow simple expressions [49] for the leading coefficients for rotational,

$$V_{0,1}^{\mathrm{a,b}} = Z_{\mathrm{a,b}}e^2\mathrm{d}\rho_{\mathrm{el}}^{\mathrm{a,b}}(R)/\mathrm{d}R|_{\mathrm{Re}}(3\varepsilon_0 k_{\mathrm{e}} R_{\mathrm{e}}) \tag{23}$$

and vibrational energies,

$$V_{1,0}^{\mathrm{a,b}} = Z_{\mathrm{a,b}}e^2(\mathrm{d}^2\rho_{\mathrm{el}}^{\mathrm{a,b}}(R)/\mathrm{d}R^2|_{\mathrm{Re}} - 3a_1/R_\mathrm{e}\mathrm{d}\rho_{\mathrm{el}}^{\mathrm{a,b}}(R)/\mathrm{d}R|_{\mathrm{Re}})/(12\varepsilon_0 k_\mathrm{e}) \qquad (24)$$

together with an analogous expression for electronic energy,

$$V_{\mathrm{T}}^{\mathrm{a,b}} = Z_{\mathrm{a,b}}e^2/(6\varepsilon_0 h)\rho_{\mathrm{el}}^{\mathrm{a,b}}(R_\mathrm{e}) \qquad (25)$$

in which appear protonic numbers $Z_{\mathrm{a,b}}$ of each atomic centre, harmonic force coefficient k_e, fundamental constants e, h and ε_0, and coefficient a_1 in formula 16 for internuclear potential energy. According to empirical values of coefficients $V_{\mathrm{kl}}^{\mathrm{a,b}}$ from precise spectral measurements, one would be able to evaluate, from measurement of wave numbers of vibration-rotational spectra of a particular diatomic molecular species in its isotopic variants, the electronic density at one nucleus as a function of the separation of the other nucleus if absolute values of mean squared radii were available. Such values of nuclear radii are difficult to measure because an atomic nucleus contains mass and charge in a diffuse distribution, even if that distribution be much less diffuse than for electronic charge outside a particular nucleus; hence various experiments provide disparate measures of such mean squared radii [50]. Because only differences in effective mean squared radii of nuclear charge between isotopes of atomic nuclei with the same atomic number are known with reasonable accuracy, formula 22 became rewritten [49] as

$$Y_{\mathrm{kl}}^{(0)} + Z_{\mathrm{kl}}^{\mathrm{f,a}} + Z_{\mathrm{kl}}^{\mathrm{f,b}} = U_{\mathrm{kl}}\mu^{-(2\mathrm{k}+1)/2}(1 + V_{\mathrm{kl}}^{\mathrm{a}}\delta\langle r^2\rangle_{\mathrm{aa'}} + V_{\mathrm{kl}}^{\mathrm{b}}\delta\langle r^2\rangle_{\mathrm{bb'}}) \qquad (26)$$

in which $\delta\langle r^2\rangle_{\mathrm{aa'}}$ is a difference of mean squared radii between isotope A and a selected standard isotope A$'$ of that atomic type, and analogously for atomic type B. Compiled values [50] of $\delta\langle r^2\rangle_{\mathrm{aa'}}$ are available from isotopic shifts of frequencies of optical transitions in atomic spectra, for which effects of mass and volume might be more readily disentangled than for molecular spectra into which an additional dependence on internuclear distance R enters; absolute values of nuclear radii are also available [51], subject to a qualification explained above. For hydrogen, the difference between wave numbers of Lyman α lines of ^{1}H and ^{2}H or D is 2237.955 ± 0.020 m^{-1} [52], due mostly to a difference of reduced mass; the field shift due to disparate nuclear volumes is only -0.020 m^{-1} for D relative to H, despite a formally large difference between root-mean-squared nuclear radii/ 10^{-15} m, 0.800 ± 0.020 for H and 2.096 ± 0.014 for D [53]. What matters for the extent of the field shift is clearly the mean squared radius of nuclear charge, rather than merely the cross section of nuclear volume. Evaluating the gradient of electronic density with internuclear distance at equilibrium separations for a few chalcogenide compounds of lead, and halide compounds of thallium, on the basis of measured rotational energies, Tiemann et alii [45] discovered an approximately linearly decreasing trend for this property. These authors mention [45] also that for a field shift to be significant as a contribution to the total isotopic effect requires a mass number of an atomic nucleus greater than 40, such as Ca with atomic number $Z=20$; the smallest mass numbers for which a field shift has been detected in diatomic molecules pertain to tin, $Z=50$, mass number $A \sim 120$ [49]. For compounds of Pb and Tl the largest contribution to isotopic effects arises from the variation of the volume or shape of nuclear centres on isotopic substitution, such that for those elements the effects of volume variation are several times the magnitude of expected effects of mass variation in the auxiliary coefficients Z_{kl} [49]. Because only relative shifts are observable, precise spectral data for at least three isotopes of a given element in a particular diatomic molecular species are required to yield information on these field shifts.

For molecules containing light atoms, we accordingly neglect this effect of finite nuclear volume or field shift, but other effects prevent exact application of isotopic ratios that one might expect on the basis of a proportionality with $Y_{kl}^{(0)}$ in formula 13 instead of total Y_{kl}. For this reason we supplement term coefficients Y_{kl}^{i} in formula 8 for a particular isotopic species i with auxiliary coefficients Z_{kl}^{i} [54],

$$E_{vJ}^{i} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}(Y_{kl}^{i} + Z_{kl}^{i})(v + 1/2)^{k}[J(J+1)]^{l} \tag{27}$$

separate from Z_{kl}^{f} above for the effect of finite nuclear volume. We moreover distinguish two contributions to these further auxiliary coefficients – those, Z_{kl}^{r}, that are required to obtain accurate applications of inter-relations, such as those in formulae 10 and 11, between term coefficients Y_{kl} of a single isotopic variant subject to restriction to leading terms $Y_{kl}^{(0)}$, and those, Z_{kl}^{v}, that become observable only on comparing parameters from spectra of isotopic species. These auxiliary coefficients furthermore become partitioned into contributions from each separate atomic type, A or B in diatomic molecule AB. With such an expansion and apart from the field shift or effect of finite nuclear volume, we rewrite the preceding formula as [55]

$$E_{vJ}^{i} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}(Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b})(v + 1/2)^{k}[J(J+1)]^{l} \tag{28}$$

in which all term coefficients on the right side pertain implicitly to a particular isotopic variant. As an effective hamiltonian for nuclear motion in formula 14 suffices to yield term values according to Dunham's formula, 8, involving only coefficients Y_{kl}^{i}, we require further terms in another hamiltonian, which might be in the form of corrections because each component of Z_{kl}^{i}, and all components in total, are typically much smaller than corresponding Y_{kl}^{i}. We remedy this deficiency by including at least one correction for each term in an effective hamiltonian, formula 14,

$$\begin{aligned}\mathcal{H}(R) = {} & \hat{p}(1 + g_{v}(R)m_{e}/m_{p})\hat{p}/(2\mu) + (1 + g_{r}(R)m_{e}/m_{p})\hbar^{2}J(J+1)/(2\mu R^{2}) \\ & + \mathrm{V}(R) + \mathrm{V}'(R) + \mathrm{V}''(R)\end{aligned} \tag{29}$$

in which g_v and g_r are called respectively vibrational and rotational g factors, and m_e and m_p are rest masses of electron and proton respectively; $\mathrm{V}'(R)$ is an analogous correction to the internuclear potential energy $\mathrm{V}(R)$. $\mathrm{V}''(R)$ is a further correction of which we allude merely to its dependence on atomic mass.

The rotational g factor relates to the fact that a free molecule acquires a magnetic dipolar moment as a result of molecular rotation [56]. Of seven terms in this expanded effective hamiltonian, for only the rotational g factor can experimental information be derived separately from other effects: for instance, for a pure rotational transition of a diatomic molecule in electronic state $^1\Sigma$ from the rotationless state with $J=0$ to a state with $J=1$, one line in absence of a magnetic field becomes a triplet, with the two additional lines displaced in frequency symmetrically and proportional to the density B of magnetic flux; the essential factor of proportionality is the rotational g factor, specifically an expectation value, $\langle J=1|g_r(R)|J=1\rangle$, of a radial function $g_r(R)$ for that rotational state, which might have a positive or negative sign. From the influence of a magnetic field on transport properties of a gaseous substance – specifically the direction of transverse transport of thermal energy or momentum, the sign of g_r is derivable [57], which task is difficult through application of the Zeeman effect on spectra unless circularly polarized radiation be applied; results of these signs were reported for diatomic species N_2, CO, HD, O_2 and NO [58], for which the sign pertains to a value of g_r averaged over rotational states occupied at the temperature of measurements. Apart from other experiments described previously [56], even estimates of the magnitude of g_r as well as sign are obtainable from measurements of thermal conductivity and shear viscosity for a gaseous substance in absence and presence of a magnetic field, plus other information; this method has been implemented for N_2 and CO [59]. For the vibrational g factor there exists no magnetic effect of low order that might provide direct experimental measurement [60].

Theoretical calculation of any atomic or molecular property through application of computational methods based on quantum mechanics or other sophisticated approach is typically practicable through approximate methods. The internuclear potential energy $V(R)$ independent of mass is conventionally derived from the results of computations of molecular electronic structure according to a scheme of wave mechanics,

$$-\left\{(\hbar^2/2m_e)\sum_{j=1}^{N}\nabla_j^2 + (e^2/4\pi\varepsilon_0)\left(-\sum_{j=1}^{N}(Z_a/r_{a,j}+Z_b/r_{b,j}) + \sum_{j=1}^{N}\sum_{l>j}^{N}1/r_{i,j} + Z_aZ_b/R\right)\right\}$$
$$\times\Psi(r_j;R) = W(R)\Psi(r_j;R) \tag{30}$$

in which $r_{a,j}$ denotes a distance between atomic nucleus A and electron j, and $r_{b,j}$ analogously for nucleus B, $r_{i,j}$ is an interelectronic distance, and $\psi(r_j;\,R)$ is an assumed total wave function for motion of N electrons with a parametric dependence on fixed internuclear distance R; we neglect magnetic effects in this formula. The total energy $W(R)$ of a molecular system, including coulombic repulsion between atomic nuclei, with these nuclei fixed at a separation R thereby becomes a potential energy $V(R)$ for the relative motion of these nuclei, according to an effective hamiltonian approximately in formula 14 or accurately in formula 29. Such an ansatz based on a formal crude separation of electronic and nuclear motions was first described by Born and Oppenheimer [61] in1927, to justify expressing a molecular energy as an approximate sum of separate contributions from rotational and vibrational motions of atomic nuclei and electronic motions. Expressing energies in such a sum had been practised implicitly for some years before this treatment appeared, and Born subsequently sought an improved derivation [62]; since that time many attempts to improve the analysis of molecular energies have been made, notably those by Longuet-Higgins through a variational principle [63] and by Fernandez [64] through application of perturbation theory, but a comprehensive analysis including both vibrational and rotational nuclear motions with electronic motions is still lacking.

Including explicitly both electronic and nuclear motions, Schrodinger's equation has never been solved exactly, even for an isolated hydrogen atom; approximate numerical solutions of an entire molecular system, involving integration over both electronic and nuclear coordinates, would yield all feasible energies of discrete and continuous states with no vestige of molecular structure in a traditional sense [65]. An intermediate approach, as incorporated in formula 29 above, involves treating atomic nuclei first as having infinite mass, thus denied kinetic energy, and solution of electronic energies on that basis. Relaxing that criterion to finite mass requires various corrections that affect, to a greater or lesser degree, energies accessible to a particular isotopic species, depending on those masses. A function $\mathrm{V}'(R)$ constitutes a correction called adiabatic because it involves calculation with wave functions of only a particular electronic state of interest, hence yielding wave-mechanical expectation values of operators for nuclear momentum operating on electronic wave functions; after standard manipulation to eliminate a dependence on the position of the centre of nuclear mass [66], one expresses this correction in this general form as a radial function,

$$\mathrm{V}'(R) = -1/2\hbar^2\langle 0|\nabla_\mathrm{a}^2/M_\mathrm{a} + \nabla_\mathrm{b}^2/M_\mathrm{b}|0\rangle \tag{31}$$

in which ∇_a or ∇_b is a differential operator with respect to nuclear coordinates that operates on the electronic wave function. This formula includes approximations: 0 denotes an electronic wave function $\psi(r_\mathrm{j};\, R)$ for the electronic ground state that is a solution of equation 29 applicable to infinite masses, and atomic masses M_a and M_b appear instead of respective nuclear masses. For that adiabatic correction in $\mathrm{V}'(R)$, the ratio of its magnitude to that of internuclear potential energy $\mathrm{V}(R)$ is clearly of order a ratio m_e/M of electronic mass to mean atomic mass M [30], hence 5.5×10^{-4} at most for a typical molecular species. Because both rotational $\mathrm{g}_\mathrm{r}(R)$ and vibrational $\mathrm{g}_\mathrm{v}(R)$ factors that appear in formula 29 have as coefficient a ratio of electronic and protonic masses, with these g factors having magnitudes of order unity at most, these terms are likewise smaller than their addend unity by a factor $\sim 5\times10^{-4}$. The ratio of the magnitude of the most important parts of contributions $\mathrm{V}''(R)$, described as nonadiabatic because they involve matrix elements of operators for linear and angular momentum between an electronic ground state of interest and electronically excited states, to $\mathrm{V}(R)$ is of order a squared ratio [67] of electronic mass and mean atomic mass, $(m_\mathrm{e}/M)^2$, hence 3×10^{-7} at most for a stable molecular species and negligible except in relation to spectral data having atypically great precision. These various corrections present in formula 29 beyond terms in formula 14 affect rotational and vibrational contributions to molecular energies in disparate manners; within a context of that effective hamiltonian, the recognition and disentangling of these contributions during spectral analysis constitutes a major challenge.

Although Herzberg [6, page 230] illustrated pictorially how *L uncoupling* might affect the energies of rotational states, it is unclear how such an explanation might be directly applicable quantitatively to vibration-rotational spectra. The fact is that, in absence of further coefficients Z_{kl}, values, for $l > 1$, of Y_{kl} of a particular isotopic species derived from precise measurements of spectra in which appear no explicit multiplets implied in Herzberg's diagram deviate significantly from those expected on a basis of $Y_{k,0}$ and $Y_{k,1}$; these systematic deviations constitute a basis for distinction of Z^{r}_{kl} from Z^{v}_{kl}, such that for diatomic molecules with like nuclear charges, for which $Z_a = Z_b$, and for hydrides, for which the atomic number of the other atomic centre much exceeds unity, some values of Z^{r}_{kl} for $l > 1$ might be derived or estimated from spectra of only one isotopic species [55]. By definition, values of Z^{r}_{kl} with $l = 0$ vanish. Values of Z^{v}_{kl} are derivable experimentally through analysis of spectra of isotopic variants; for a reasonably significant evaluation of several values of both Z^{v}_{kl} and Z^{r}_{kl}, numerous spectral data for isotopic variants of both atomic types over the same range of energy as for a principal isotopic species are essential. A presence either of a ratio m_e/m_p as factor of radial functions for rotational and vibrational g factors or of a ratio of electronic to nuclear masses implicitly within adiabatic corrections $V'(R)$, as explained above, implies that auxiliary term coefficients Z_{kl} that have their source in such effects have magnitudes much smaller than those of dominant term coefficients $Y^{(0)}_{kl}$, and nonadiabatic corrections $V''(R)$ even smaller; typically $Z_{kl} \sim Y^{(2)}_{kl}$ and effects of $V''(R)$ would be $\sim Y^{(4)}_{kl}$. A further contribution Z^{f}_{kl} to total auxiliary term coefficient Z_{kl} that is due to an effect of nuclear volume or field shift, and proportional to $V^{a}_{kl}\delta\langle r^2\rangle_{aa'}$, from formula 26, might have a magnitude comparable with contributions from mass effects for atoms of large atomic number, as mentioned above.

For a particular isotopic variant of a diatomic molecule with like charges on atomic centres, i.e. $Z_a = Z_b$, and for which we assume no net molecular electric dipolar moment at any internuclear distance, i.e. $p(R) = 0$ for all R, we hence express the coefficient of $(v + \frac{1}{2})^k\ [J(J+1)]^l$ in formula 27 as a sum,

$$Y_{kl} + Z^{v}_{kl} + Z^{r}_{kl} + Z^{f}_{kl} \tag{32}$$

The rotational and vibrational g factors have a dependence [66] on masses of atomic centres of forms

$$g_r(R) = m_p g^{irr}_r(R)[1/M_a + 1/M_b] = g^{irr}_r(R) m_p/\mu \tag{33}$$

$$g_v(R) = m_p g^{irr}_v(R)[1/M_a + 1/M_b] = g^{irr}_v(R) m_p/\mu \tag{34}$$

in which $g^{irr}_r(R)$ and $g^{irr}_v(R)$ contain electronic contributions regarded to pertain to irreducible nonadiabatic functions pertaining to rotational and vibrational motions [66], respectively. Simplified from formula 31, the adiabatic correction becomes analogously expressed compactly as

$$V'(R) = -1/2\hbar^2\langle 0|\nabla_a^2|0\rangle/\mu \tag{35}$$

because $\nabla_a^2 = \nabla_b^2$. Because field shifts between isotopic nuclei have their source in significant differences between distributions of nuclear charges in space, or nuclear volume, no comparable compacting of expression is practicable for this effect; formulae 22 and 26 remain applicable to a species with $Z_a = Z_b$ just as for $Z_a \neq Z_b$.

For a diatomic molecule with unlike charges on atomic centres, so $Z_a \neq Z_b$, we express the coefficient of $(v+½)^k\ [J(J+1)]^l$ in formula 27 as a sum of seven addends,

$$Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b} + Z_{kl}^{f,a} + Z_{kl}^{f,b} \tag{36}$$

The rotational and vibrational g factors of net electrically neutral molecule $^-AB^+$ with an indicated electric polarity show a dependence [66] on masses of atomic centres of forms

$$g_r(R) = [g_r^{irr}(R) - p(R)/(eR)]m_p/M_a + [g_r^{irr}(R) + p(R)/(eR)]m_p/M_b \tag{37}$$

$$g_v(R) = [g_v^{irr}(R) - (1/e)dp(R)/dR]m_p/M_a + [g_v^{irr}(R) + (1/e)dp(R)/dR]m_p/M_b \tag{38}$$

in which p(R) denotes a radial function for electric dipolar moment, and dp(R)/dR its first derivative with respect to internuclear distance. Formulae 37 and 38 exhibit a partition of total nuclear and electronic contributions to rotational and vibrational g factors into contributions of separate atomic centres [66] in a neutral molecule that is consistent with their expression in this more compact form,

$$g_r(R) = g_r^{irr}(R)m_p/\mu - m_p[1/M_a - 1/M_b]p(R)/(eR) \tag{39}$$

$$g_v(R) = g_v^{irr}(R)m_p/\mu - (m_p/e)[1/M_a - 1/M_b]dp(R)/dR \tag{40}$$

Electronic contributions to $g_r(R)$ and $g_v(R)$ relate to nonadiabatic rotational and vibrational effects, respectively, as electronic matrix elements [9], whereas a nuclear contribution, the same in each case,

$$g_r^{nuc} = g_v^{nuc} = m_p(Z_aM_b/M_a + Z_bM_a/M_b)/(M_a + M_b) \tag{41}$$

simply depends on atomic numbers and atomic masses, independent of internuclear distance [66]. Scrutiny of the applicable quantities reveals that this nuclear contribution can adopt only a positive value, whereas the total electronic contributions to both $g_r(R)$ and $g_v(R)$ have invariably negative values; the sign of the net value of $g_r(R)$ or $g_v(R)$ hence depends on the relative magnitudes of these negative and positive contributions. The total adiabatic corrections can assume both negative and positive values. For a diatomic molecule with $Z_a \neq Z_b$, the corresponding adiabatic correction is given simply in its general form, formula 31, and formula 26 is applicable to the relative field shift.

4. BASIS OF APPLICATION OF DUNHAM'S AND VAN VLECK'S THEORY TO ANALYSIS OF DIATOMIC SPECTRA

Bearing in mind that the primary objective of spectral analysis in its two stages combined is to evaluate parameters of minimal number that serve to reproduce archetypal characteristics of spectral lines in related sets, we consider how to apply formulae presented above for analysis of data of type wave number or frequency of spectral transitions. On a purely empirical basis for spectra of each separate isotopic species, one might simply apply formulae 2 and 3 in combination,

$$\tilde{\nu} = \sum_{k=0} \sum_{l=0} A_{\mathrm{kl}} \{ (v' + 1/2)^k [J'(J' + 1)]^l - (v'' + 1/2)^k [J''(J'' + 1)]^l \} \tag{42}$$

For many values of wave number $\tilde{\nu}$ for diverse transitions within a particular range of quantum numbers v and J to yield a few values of phenomenological parameters A_{kl} for each separate isotopic variant, a standard statistical treatment to evaluate these over-determined parameters involves merely linear regression, best performed according to a criterion of least sum χ^2 of squares of residuals; a residual is a difference between a measured value of $\tilde{\nu}$ and the corresponding value calculated with A_{kl} in a given set. This treatment, like all succeeding improvements thereon, is naturally amenable to weighting of each measured wave number to take into account a variable ratio of signal to noise among spectral lines in a set, partial overlap of lines et cetera. For typical vibration-rotational data in a collection for a particular species, the most important parameters A_{kl} are those pertaining to vibrational energies, $A_{\mathrm{k,0}}$, and those pertaining to rotational energies, $A_{\mathrm{k,1}}$; additional parameters of type $A_{\mathrm{k,2}}$, $A_{\mathrm{k,3}}$ … related to centrifugal distortion are typically added empirically to a set under test until further addition of parameters yields no diminution of χ^2. As a rough guide to the extent of parameters of type $A_{\mathrm{k,0}}$, for data extending over a typical range from $v=0$ to v_{max} the corresponding maximum level of $A_{\mathrm{k,0}}$ would have $k=v_{\mathrm{max}}$; especially for diatomic species other than hydrides, such an extent of $A_{\mathrm{k,0}}$ is unlikely to be required, and the maximum value of k might be only ½ v_{max}. The range of parameters of type $A_{\mathrm{k,1}}$ is likely to require a maximum value of k the same as, or one unit less than, is required for parameters of type $A_{\mathrm{k,0}}$, and several further $A_{\mathrm{k,2}}$, $A_{\mathrm{k,3}}$, $A_{\mathrm{k,4}}$ … might be judiciously included for smaller k.

In an analogous manner, this approach is extensible to treat simultaneously data of multiple isotopic variants of a particular diatomic species; such a treatment might be based on application of differences of spectral terms according to formula 19, with empirical parameters B_{kl} and $\Delta_{\mathrm{kl}}^{\mathrm{a,b}}$ therein as explained at that point. In such a treatment there is convenience in distributing a factor reduced mass μ between vibrational and rotational quantum numbers, or rather their respective functionals, in the following form, known as *mass-reduced quantum numbers* [68],

$$(v + 1/2)/\mu^{1/2}, \quad [J(J + 1)]/\mu \tag{43}$$

Hence these functionals of quantum numbers v and J become compounded with reduced mass μ; differences of these quantities to various powers k and l that serve as regressors no longer retain integer values, respectively, for molecules in electronic state of class $^1\Sigma$ or 0.

As mentioned above, reduction of spectral data in terms of such empirical parameters A_{kl}, or B_{kl} and $\Delta_{kl}^{a,b}$, achieves an objective of this process, namely that those parameters number appreciably fewer than the number of fitted wave numbers $\tilde{\nu}$ of separate transitions. One obtains further reduction on applying constraints to freely adjustable parameters A_{kl}, or $B_{kl,}$ to convert them to Dunham coefficients Y_{kl}, or $U_{kl,}$ respectively. One might even retain linear regression in this process, implying that initial estimates of parameters are not required, according to an iterative approach that Tiemann developed [69]: in the first iteration, parameters A_{kl}, or B_{kl} and $\Delta_{kl}^{a,b}$, are freely adjustable within a selected set defined by subscripts k and l, and coefficients a_j for potential energy according to Dunham's formula 16, or some equivalent such as b_j or c_j coefficient of y or z respectively in formulae 20 and 21, are subsequently evaluated from $A_{k,0}$ and $A_{k,1}$. In the next iteration these values of coefficients for potential energy are substituted into expressions for Y_{kl} with $l > 1$, and the corresponding contributions $Y_{kl}^{i}(v + 1/2)^k[J(J + 1)]^l$ with $l > 1$ to spectral terms E_{kl}^{i} are subtracted from those terms; the remaining parts of those terms are refitted to define further values of coefficients a_j for potential energy. This iterative process is continued until convergence, or self consistency, of values of coefficients for potential energy according to an appropriate criterion. One consequently obtains, with empirical parameters $\Delta_{kl}^{a,b}$, Dunham coefficients Y_{kl}^{i}, or their equivalent quantities U_{kl} formally independent of nuclear mass, in a set from $Y_{0,0}$ to $Y_{k,0}$ and $Y_{0,2k}$ consistent with coefficients a_j, or convenient alternative such as c_j, up to some maximum level of j. Further coefficients Y_{kl}^{i} are taken to be zero according to truncation of infinite sums in formula 8 necessitated by spectral data having finite number, whereas further coefficients a_j, or alternative, have values entirely indeterminate, but which are unlikely to be zero. By inserting published values of parameters a_j into known expressions of term coefficients Y_{kl}^{i}, one can satisfy oneself that this criterion of consistent truncation of sums in formula 8 has been practised such as in work on HBr [37] and HCl [36] since the commencement of efforts to employ Dunham's formulae for Y_{kl}^{i} in a consistent manner; although such a criterion is only implicit within Dunham's paper [5], it has nevertheless been essentially universally applied; insinuation of further primary quantities Y_{kl}^{i} with non-zero values other than those supported directly by the data set into a treatment of data in a particular set beyond that implied by subsidiary parameters such as a_j or c_j to a specific level is recognised to be incongruous.

On the basis of this criterion one might attempt to estimate some further subsidiary parameters, according to the following scheme [69]. If the fitted value of a_j of ultimate order j be even, with value m for instance, that condition implies a non-zero value of some Dunham coefficient $Y_{k,0}$ of largest value of k, such as n, and thereby other coefficients $Y_{n-1,2}$, $Y_{n-2,4}$ … with even l, and other coefficients $Y_{n-1,1}$, $Y_{n-2,3}$ … with odd l. One might then estimate a_{m+1} from a formula for $Y_{n,1} = 0$, or alternatively from $Y_{n\text{-}1,3} = 0$, or analogously for other Y_{kl} with lesser k but increasing odd values of l. This operation fails to yield consistent results because that estimate of a_{m+1} from $Y_{n,1} = 0$ likely differs significantly from the corresponding estimate from $Y_{n\text{-}1,3} = 0$. One might argue that one should prefer the former value because it arises from an assumption that a principal Dunham coefficient $Y_{n,l}$ with $l=0$ or 1 has a zero value, but such an argument involves an arbitrary selection. In any case, further such application of this scheme, to yield an estimate of a_{m+2} from $Y_{k+1,0}$ and so forth, rapidly leads to divergent and unphysical magnitudes of these parameters a_j, such that this scheme becomes impracticable and unreliable [70], like any other contrivance to extrapolate in lack of both an exact model and exact data. Whether the above argument involves Y_{kl} or their equivalents U_{kl} independent of mass, which would be actually employed in reduction of spectral data of multiple isotopic variants, is immaterial: the same conclusion follows.

Although a traditional approach without Tiemann's extension [69] yields parameters a_j of minimum number, which hence imply primary coefficients Y_{kl} of minimum number in a consistent set, there remain empirical parameters $\Delta_{kl}^{a,b}$ that might have their number reducible through their expression to radial coefficients in functions for extra-mechanical effects – such as $g_r(R)$, $g_v(R)$ and $V'(R)$ introduced above. A few approximate relations such as [71]

$$\Delta_{0,2} \approx 3\Delta_{0,1} - 2\Delta_{1,0} \tag{44}$$

have been derived, but a more systematic approach in terms of those radial functions is clearly required. Although, on the basis of application of a JBKW approach [26], formulae were derived to relate quantities equivalent to $V'(R)$ and $g_r(R)$ in an effective hamiltonian, formula 29 apart from V'', without g_v, a full solution including $g_v(R)$ beyond a constant term awaited development of hypervirial perturbation theory and its application first to derivation of Dunham coefficients Y_{kl} [28], and subsequently to auxiliary term coefficients Z_{kl} [72]. Employing an effective hamiltonian [66] in an alternative form in formula 29 above that is equivalent to that applied in that derivation [72], and observing that, on a basis of formulae 34, 33 and 31, these extra-mechanical effects are expressible in terms of sums of contributions involving reciprocal masses M_a and M_b of separate neutral atoms [66], we postulate the following radial functions for vibrational and rotational g factors and adiabatic corrections, respectively, in terms of reduced displacement variable z defined in formula 21:

$$g_v(R) \rightarrow g_v(z) = m_p\left(\sum_{j=0} s_j^a z^j / M_a + \sum_{j=0} s_j^b z^j / M_b\right) \tag{45}$$

$$g_r(R) \rightarrow g_r(z) = m_p\left(\sum_{j=0} t_j^a z^j / M_a + \sum_{j=0} t_j^b z^j / M_b\right) \tag{46}$$

$$\mathrm{V}'(R) \rightarrow \mathrm{V}'(z) = hcm_e\left(\sum_{j=0} u_j^a z^j / M_a + \sum_{j=0} u_j^b z^j / M_b\right) \tag{47}$$

This formulation [72] includes terms only linear in a ratio m_e/M_a of electronic and atomic masses. Whereas coefficients c_j pertaining to potential energy, or their counterparts a_j in Dunham's expressions [5], occur non-linearly in Dunham coefficients Y_{kl}, as exhibited in this instance,

$$Y_{2,1} = (B_e^3/\omega_e^2)(45c_1^3 + 27c_1^2 - 78c_1c_2 + 30c_3) + \ldots \qquad (48)$$

in which B_e and ω_e are primary rotational and vibrational parameters appearing in formulae 6 and 5 respectively, coefficients $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ occur only linearly in auxiliary coefficients Z_{kl}^v or Z_{kl}^r for either atomic type in formula 28, as this instance demonstrates.

$$Z_{1,0}^{v,a} = 1/2\ \omega_e s_0^a m_p/M_a + 2(B_e/\omega_e)[u_1^a(1 - 3c_1/2) + u_2^a]m_e/M_a \qquad (49)$$

Despite the linear occurrence of $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ among themselves, they occur in products with other parameters c_j, B_e and ω_e; the latter two quantities each separately contain, implicitly, reduced mass, as μ^{-1} in B_e and $\mu^{-1/2}$ in ω_e through these explicit formulae,

$$B_e \equiv h/(8\pi^2 c\mu R_e^2) \qquad (50)$$

$$\omega_e \equiv (k_e/\mu)^{1/2}/(2\pi c) \qquad (51)$$

consistent with formula 13. These two quantities constitute convenient forms to represent parameters R_e and c_0, which belong to $V(z)$ according to a definition of z in formula 21 and the following explicit formula,

$$V(R) \to V(z) = V_0 + hcc_0 z^2\left(1 + \sum_{j=1} c_j z^j\right) \qquad (52)$$

with

$$c_0 = a_0 \equiv \omega_e^2/(4B_e) = 1/2\ k_e R_e^2/hc \qquad (53)$$

The right sides of both latter expressions evidently contain no dependence on mass, and formula 52 is analogous to formula 16. Consistent with use of reduced quantum numbers according to formulae 43, in practice $U_{1,0}$ replaces ω_e and $U_{0,1}$ replaces B_e during fitting of spectral data with mass-reduced quantum numbers. Inversion of spectral data to coefficients c_j, $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ and R_e in pertinent radial functions to represent in a compact form, according to an ultimate spectral reduction, Dunham coefficients Y_{kl} and auxiliary coefficients Z_{kl} in sets consistent with radial coefficients at particular levels clearly requires estimation of non-linear parameters in the form of those radial coefficients. The first algorithm to achieve this objective is embodied in a Fortran programme for weighted non-linear regression called Radiatom [55], in which a main routine serves to specify masses and to read data; its call also of a subroutine [73] initiates activity of an efficient fitting algorithm according to a method that Newton originated and that Levenberg, Marquardt, Choleski, Hammarling, Morrison, Osborne [73] and others developed subsequently. That subroutine in turn calls another subroutine that calculates both the wave numbers of transitions, according to fixed values of regressors – masses of atoms constituting a particular isotopic variant and quantum numbers of lower and upper states of an assigned transition in a list in the data set – and adjusted or constrained values of parameters – radial coefficients or associated quantities as explained above, and the derivatives of residuals with respect to those parameters. The wave number of each transition is calculated directly through Dunham, Y_{kl}, and auxiliary coefficients, collectively Z_{kl}, as in

$$\begin{aligned}\tilde{\nu} = \sum_{k=0}\sum_{l=0}(Y_{\mathrm{kl}} + Z_{\mathrm{kl}}^{\mathrm{v,a}} + Z_{\mathrm{kl}}^{\mathrm{v,b}} + Z_{\mathrm{kl}}^{\mathrm{r,a}} + Z_{\mathrm{kl}}^{\mathrm{r,b}})\{(v' + 1/2)^k[J'(J' + 1)]^l \\ - (v'' + 1/2)^k[J''(J'' + 1)]^l\}\end{aligned} \tag{54}$$

These coefficients Y_{kl} and collectively Z_{kl} are employed precisely as the primary quantities according to the theory of Dunham [5] and van Vleck [9], calculated through their expressions in terms of radial parameters in other subroutines; those many expressions have simply the forms shown in formulae 48 and 49 above. Their radial coefficients serve to maintain a consistent level of Y_{kl} and each component of Z_{kl}. Further subroutines of Radiatom contain expressions for derivatives of these primary quantities with respect to radial coefficients. Symbolic expressions for derivatives of residuals with respect to radial parameters enable fitting more efficient than merely numerically calculated derivatives, through first or second finite differences; such symbolic derivatives in a fitting procedure facilitate convergence, and hence require initiate estimates of parameters less near the ultimately fitted values than for numerical derivatives. All these expressions in these subroutines were initially formed directly with symbolic processors Reduce and Maple, through automatic generation of Fortran code, and are evaluated with numerical precision of calculations set at 32 decimal digits. With increasing speed of computer hardware and increasing sophistication of software, generation of expressions for Y_{kl} and various Z_{kl} with Maple and subsequent utilisation of these expressions in a separate fitting procedure entirely within Maple that evaluates selected radial coefficients according to another procedure also based on work of Levenberg and Marquardt has become feasible; Radiatom II functions in this manner, with precision readily selectable but set typically at 24 decimal digits. Taking full advantage of use of software for computer algebra, a novel feature of the latter procedure is utilisation therein of symbolic differentiation of an algebraic procedure (M. B. Monagan and J. F. Ogilvie, in preparation) that builds a grand expression for $E_{\mathrm{vJ}}^{\mathrm{i}}$ through a sum of Y_{kl} and all appropriate components of Z_{kl}. Operation of Radiatom II is practical for data in a set numbering less than 500; such a computation to converged parameters involves typically a duration up to 2000s, relative to as little as 90s for data and parameters in the same sets and the original Radiatom in Fortran with a powerful processor; the difference reflects that Fortran programmes are fully compiled, whereas Maple procedures employ compiled numerical subroutines but operate at the top level in an interpreted manner, hence slowly. Although estimated standard errors of parameters and coefficients of correlation between parameters are practically identical for analyses of the same data with Radiatom in these two versions, the converged values of parameters are not quite identical but agree within the stated errors. Extensive vibration-rotational data in appropriate sets of which an analysis might involve effects of finite size of atomic nuclei are lacking; for neither Radiatom nor Radiatom II has there been made an attempt to encompass these effects. For both procedures typically 10–20 iterations are required to reach convergence according to a specified criterion.

For Radiatom, upon approach to convergence, that criterion involves a test that involves the sensitivity of parameters to adjustment; ample experience with Radiatom has demonstrated that this test fails if initial estimates of adjusted parameters, typically numbering 10–25, are near the finally converged values. This peculiarity has led to use of deliberately rough values of $U_{1,0}$ and $U_{0,1}$ with characteristic standard values of c_1 and c_2 as initial estimates [13, table 4.26]; initial estimates of all other values of adjustable parameters are entered as zero. For this reason the initial value, for both Radiatom and Radiatom II, of a sum of weighted residuals, χ^2, is typically of order 10^{15}, eventually decreasing to a value typically of order 10^4 at convergence; during this process values of parameters sample a large area of the hypersurface of χ^2, and local minima seem to be avoided in favour of an apparent global minimum, at least within a physically reasonable domain of parameter space. For this reason also a deliberate attempt to seek a local minimum of χ^2, or otherwise to influence the ultimate values of parameters, is impracticable; the process of evaluating parameters, within a particular set, thus becomes as objective as practicable within a limitation of necessarily providing initial estimates of parameters as dictated by the nature of non-linear regression. A further property of Radiatom is its inability to fit linearly dependent parameters; an error message “Parameter … is linearly dependent upon previous parameters” appears on initiating any attempt of this type, and execution terminates at that point, generally at the first iteration. Experience with Radiatom II is less extensive than with the original Radiatom, but similar behaviour seems to apply; this manner of performance might be a general feature of regression according to the algorithm of Levenberg and Marquardt when applied to many parameters.

5. APPLICATIONS OF DUNHAM’S FORMALISM TO SPECTRAL ANALYSIS

As an objective, spectral reduction involves evaluating parameters of minimal number that serve to reproduce wave numbers of transitions within, on average, their precision of measurement. According to an approach based on the formalism of Dunham and its extension by van Vleck, one seeks hence to evaluate term coefficients Y_{kl} and various Z_{kl} in sets that are both minimal and consistent, achieving the latter property through secondary parameters of some appropriate kind. Although Dunham’s original derivation involved a function V(x) and its parameters a_j, an alternative scheme has generated as its result exactly formula 2 above incorporating Y_{kl}^{GCA}; instead of potential energy and kindred radial functions this generator-coordinate approach [74,75] involves integral kernels prospectively obtained from calculations of molecular electronic structure and matrix elements of nuclear operators, hence directly transcending the crude approximation resulting from formula 30. One can not emphasise too strongly that a radial function, such as V(R) for potential energy or p(R) for electric dipolar moment that according to conventional treatments is taken to govern wave numbers or strengths, respectively, of lines associated with typical transitions measured in infrared spectra, is an artefact of a formal separate treatment, which is approximate, of electronic and nuclear motions; notwithstanding this global truth, one includes further radial functions that serve as corrections, such as those in formula 29 beyond terms in formula 14, to improve reproduction of experimental data by transcending somewhat that approximation when such corrections are sufficiently small to be considered acceptable perturbations. There exists hence at least one fully theoretically justified alternative to use of radial functions that have as argument either directly internuclear distance R or a functional of R in combination with R_e. In sum, a radial function such as potential energy is an artefact of a theoretical ansatz – an artificial distinction between motions of subatomic particles unjustifiable according to rigorous quantum mechanics even though quantum-mechanical methods might serve to calculate applicable quantities in a semi-classical approach. A radial function is not an experimentally observable quantity, and is not even essential to the practice of Dunham's formalism in analysis of molecular spectra. Furthermore, since Dunham's time proof has existed [76,77] that inversion of spectral data involving only bound states fails to define uniquely a function for potential energy, with or without auxiliary functions for adiabatic corrections, vibrational and rotational g factors et cetera. A simple example of such lack of uniqueness exists for equal differences between adjacent vibrational energies: the number of corresponding functions for potential energy is uncountable [78,13]. To evaluate V(R) uniquely from data pertaining to only a particular angular momentum, one requires also knowledge of phase shifts of all continuum states [79], although scattering data at fixed energy enable recovery of potential energy [80]. The essential raison d'etre of a radial function is precisely to ensure that Dunham coefficients, Y_{kl} extended with various Z_{kl}, comprise a consistent set of minimal number, in accordance with the principle of parsimony or Occam's razor, thus allowing one to achieve maximal spectral reduction; the underlying evaluated radial parameters or prospective integral kernels incidentally also number minimally within a consistent set. These Dunham coefficients, independent of any model that inter-relates them such as a function for potential energy or integral kernels based on a generator coordinate, constitute a systematic representation, through formula 54 as extended to include effects of nuclear volume if necessary, of actual or feasible measurements of wave numbers of spectral lines within a range of quantum numbers v and J for which values of these coefficients are valid.

Notwithstanding the preceding fundamental verity, one discerns qualitative similarities between features of these radial functions and observable quantities from other than spectral experiments. For instance, a value of the hypothetical equilibrium internuclear distance R_e deduced from spectra of gaseous CO in its electronic ground state is similar to a value of interatomic distance derived from crystallographic data obtained in experiments with diffraction of xrays, and expected to be similar also for deductions from experiments with diffraction of electrons or neutrons, even though the latter three experiments might yield significant variation of that parameter even for samples measured at the same temperature and state of aggregation. Moreover, one expects that radial functions derived from disparate methods of spectral reduction of data in a common set likely exhibit similar characteristics and trends, although there is no reason to envisage exact agreement.

How does one proceed to evaluate Dunham coefficients Y_{kl} and Z_{kl} from spectral data comprising transitions combining several vibrational and many rotational states of a particular diatomic molecular species in multiple isotopic variants? We here assume that assignments of all transitions in terms of v and J of combining states are already made, although in practice it is entirely feasible to undertake an analysis of spectra of a particular species involving making such assignments for a selected subset of measured lines and using tentative values of both Y_{kl} consistent with underlying parameters such as a_j or c_j to extend assignments. Such a procedure has been applied, for instance, in analysis of spectra of vapours of RbCl [81] and GeO [82] in absorption. If parameters be evaluated for individual bands of the most abundant isotopic species, one can generally be guided to the maximum necessary value of k in $Y_{k,0}$ by fitting the origins or centres of vibration-rotational bands to a polynomial in $v + \frac{1}{2}$ in formula 5 or equivalent, and the corresponding maximum necessary value of k in $Y_{k,1}$ through an analogous fit of B_v in formula 6; for a typical collection of spectral data including vibration-rotational bands, the value of k derived from thus fitting B_v is likely within one unit of the value of k derived from fitting band origins. Such fits of individual bands are useful also to provide estimated standard deviations of wave numbers that can serve as weights in the ensuing regression to evaluate radial and Dunham coefficients. In lack of such guidance, a direct fit of an entire set of spectral data, with weights estimated from other observations, can proceed with trial selection of ranges of radial coefficients, eventually to achieve convergence and monitored with values of statistical indicators of goodness of fit. Because radial coefficients a_j or c_j for potential energy occur in algebraic formulae of Y_{kl} in a highly non-linear manner, as shown in formula 48 for instance, it is mandatory to retain all those quantities as parameters up to a particular maximum value, even though an estimated standard error of an intermediate coefficient might indicate its nominal lack of significance. Moreover, successive radial coefficients become introduced into expressions for energies of vibration-rotational states through successive orders according to perturbation theory of Rayleigh and Schrodinger in hypervirial form [30] or otherwise [21]. The JBKW method with all quantum corrections yields the same series as standard quantal perturbation theory for an anharmonic oscillator [72,83,84]; hence the corresponding infinite series are identical, although each approach might generate terms in distinct manners: to have the terms identical order by order one must choose the same perturbation parameter and invert the BKW equation up to the same order chosen in quantal perturbation theory. For this reason also, it is illogical and improper to reject parameters such as a_j or c_j that occur first in a particular order of perturbation theory but to accept analogous parameters that become introduced according to this theory in a higher order. When this theory is applied in a consistent and systematic manner, the practical generation thereby of radial coefficients for potential energy in a minimal set from given frequency data, and hence of consistent parameters Y_{kl}, generally suffers from no ambiguity of extent of polynomial.

In contrast, selection of radial coefficients for extra-mechanical effects poses significant difficulty: the reason is that, even ignoring the effect of nuclear volume and of further nonadiabatic effects in $V''(R)$, these effects number three for an atomic centre of each distinct atomic number, according to parameters in formulae 45, 46 and 47, whereas auxiliary coefficients of types $Z^{\mathrm{v}}_{\mathrm{kl}}$ or $Z^{\mathrm{r}}_{\mathrm{kl}}$ number only two. Moreover, although adiabatic effects contribute to only $Z^{\mathrm{v}}_{\mathrm{kl}}$ and the rotational g factor to only $Z^{\mathrm{r}}_{\mathrm{kl}}$, parameters pertaining to the vibrational g factor appear in formulae for both $Z^{\mathrm{v}}_{\mathrm{kl}}$ and $Z^{\mathrm{r}}_{\mathrm{kl}}$, but with no net contribution to $Z^{\mathrm{v}}_{0,l} + Z^{\mathrm{r}}_{0,l}$. Without either additional information from experiments with samples in applied electric and magnetic fields or equivalent information obtained through a practice of computational spectrometry, one must either make an – at least somewhat – arbitrary selection of parameters of types s_{j}, t_{j} and u_{j}, in formulae 45, 46 and 47 respectively, or construct modified parameters in various combinations for the purpose of fitting spectra [28,85]; in either case a numerical value of such a parameter might lose its nominal *physical* significance in regard to a particular term in a hamiltonian, although the overall objective of deriving values of coefficients Y_{kl} and Z_{kl} to reproduce spectral data is unaffected.

We examine a few particular radial coefficients in detail. Coefficients $u_0^{\mathrm{a,b}}$ pertaining to adiabatic corrections in $V'(R)$ appear in only an expression for auxiliary coefficient $Z^{\mathrm{v}}_{0,0}$, explicitly in this form [55]:

$$Z^{\mathrm{v}}_{0,0} = m_{\mathrm{e}}(u_0^{\mathrm{a}}/M_{\mathrm{a}} + u_0^{\mathrm{b}}/M_{\mathrm{b}}) \tag{55}$$

Being the coefficient of $(v+½)^0\ [J(J+1)]^0$, this term $Z^{\mathrm{v}}_{0,0}$ is merely a contribution to residual energy and is indeterminate from measurements of wave numbers of spectral transitions between bound vibration-rotational states within the same electronic state. For radiative dissociation of diatomic molecule AB into atomic ions A^- and B^+, one can measure the energy with considerable accuracy, equivalent to $\sim 100\ \mathrm{m}^{-1}$ for such a diatomic molecular reactant [86]; application of this experiment to HCl and to DCl enabled measurement of a difference $(320 \pm 100)\ \mathrm{m}^{-1}$ after other differences of dissociation energy and residual energy were taken into account [86]. A possibility exists that this difference might be attributed to u_0^{H}, which implies a value $(1.2 \pm 0.4) \times 10^6\ \mathrm{m}^{-1}$ of this quantity: such a magnitude is comparable with values/$10^6\ \mathrm{m}^{-1}$ for $u_1^{\mathrm{H}} = -6.1233 \pm 0.0026$ and $u_2^{\mathrm{H}} = 18.3836 \pm 0.0097$ deduced from analysis of infrared spectra of HCl [55], although the latter value is susceptible to contamination from coefficient s_0^{H} related to the vibrational g factor for reasons explained above; explicit calculation of adiabatic corrections for HCl would verify this point. Such calculations of $Z^{\mathrm{v}}_{0,0}$ are reported for diatomic molecules H_2, HF, N_2 and F_2 [87], not HCl; a notable result of those calculations, unmentioned by the authors, is a finding that a ratio of $Z^{\mathrm{v}}_{0,0}$ to total electronic energy tends to decrease with increasing atomic number or mass. Handy and Lee investigated the effects of adiabatic corrections on "bond length" and "vibrational frequencies" of diatomic molecules [87]; these effects also decrease with increasing atomic number or mass, but for some molecules nonadiabatic effects are more important than adiabatic corrections in this context [88]. In any case, because coefficients $u_0^{a,b}$ in $V'(R)$ appear in only $Z_{0,0}^{v}$ that imposes no tangible effect on wave numbers of spectral transitions between bound states within a particular electronic state, we ignore them in further deliberations here.

Of leading radial coefficients of two other types in relation to extra-mechanical effects, $s_0^{a,b}$ pertain to the vibrational g factor, and $t_0^{a,b}$ pertain to the rotational g factor; in both cases these quantities also involve electric dipolar moment through its radial function $p(R)$, or equivalently in terms of reduced displacements x or z in $p(x)$ or $p(z)$. We express the latter in an expansion,

$$p(R) \rightarrow p(z) = \sum_{j=0} p_j z^j \tag{56}$$

according to these relations [66] applicable to a molecule of relative polarity $^{-}AB^{+}$,

$$s_0^a = \mu[g_v(R_e)/m_p - 2p_1/(eR_eM_b)] \tag{57}$$

$$s_0^b = \mu[g_v(R_e)/m_p + 2p_1/(eR_eM_a)] \tag{58}$$

$$t_0^a = \mu[g_r(R_e)/m_p - 2p_0/(eR_eM_b)] \tag{59}$$

$$t_0^b = \mu[g_r(R_e)/m_p + 2p_0/(eR_eM_a)] \tag{60}$$

which involve values of rotational and vibrational g factors, electric dipolar moment and its derivative all evaluated at R_e. If one could evaluate significantly these radial coefficients through reduction of pure rotational and vibration-rotational spectra measured for samples of a diatomic compound in the absence of applied electric or magnetic field, one might thus be able to estimate electric and magnetic properties of this molecule in the same electronic state, specifically one or other g factor and either the permanent electric dipolar moment p_0 or its gradient p_1 at the equilibrium internuclear distance [89]. Doubt has been expressed [90] about the feasibility of such a significant evaluation of t_0^a and t_0^b under those conditions, but this reservation arises from inadequate understanding of expressions for auxiliary coefficients Z_{kl}. If one consider only the total quantity $Z_{0,1}$ for an atomic centre of type A according to this relation,

$$Z_{0,1}^a = Z_{0,1}^{v,a} + Z_{0,1}^{r,a} = (B_e t_0^a + \gamma^2 u_1^a) m_e/M_a \tag{61}$$

in which $\gamma \equiv 2\ B_e/\omega_e$, and if one suppose that only the total quantity $Z_{0,1}^a$ be deducible from spectral data for a sample without applied field, radial coefficients t_0^a and u_1^a are perfectly correlated – because factors B_e and γ^2 have the same dependence on reduced mass μ – and can thus not be significantly evaluated, which is the basis of the purported argument [90]. Other relations, however, such as

$$Z_{0,2}^a = Z_{0,1}^{v,a} + Z_{0,1}^{r,a} = \{B_e[-2t_0^a + t_1^a] + \gamma^2[u_1^a(-3c_1/2 - 2) + u_2^a]\}\gamma^2 m_e/M_a \tag{62}$$

break that perfect correlation because therein t_0^a and u_1^a occur with other than unit numerical factors. If one take total auxiliary coefficients Z_{kl} up to $Z_{3,0}^a$, $Z_{2,2}^a$, $Z_{1,4}^a$

and $Z^{a}_{0,6}$ – or equivalently Δ^{a}_{kl} in formula 19 with subscripts in the same range – that number 15 in total, excluding $Z^{a}_{0,0}$, these imply radial coefficients in subsets, excluding u^{a}_{0}, up to s^{a}_{4}, t^{a}_{5} and u^{a}_{6}, hence numbering 17 variables. Unknown radial parameters thus outnumber auxiliary coefficients Z_{kl} through which the former might be evaluated in principle. For this reason not all those radial coefficients can be evaluated without supplementary information. In practice, a truncated subset would require arbitrarily discarding two selected coefficients, most reasonably two among the three, s^{a}_{4}, t^{a}_{5} and u^{a}_{6}, that derive from greatest orders of perturbation theory. Values of some remaining coefficients, at least those at the highest remaining levels, would thereby adopt a mixed character, and would accordingly lose their connection to a particular term in an effective hamiltonian and hence to a particular source of effect such as rotational or vibrational *g* factor. One expects reasonably, however, that values of radial coefficients at the least levels, such as s^{a}_{0}, t^{a}_{0} and u^{a}_{1}, would assume little or no mixed character and thus retain essentially their pure relation, apart from error of these parameters propagated from measurements of wave numbers of spectral lines, to particular terms in the effective hamiltonian, formula 29 with neglect of $V''(R)$. An objective to take these various parameters in combinations, optimal or otherwise, as fitting coefficients overcomes this indeterminacy [29,85], but at a loss of all or most correspondence between evaluated parameters and terms in that hamiltonian. To illustrate this problem we consider in detail one instance of significant evaluation of a rotational *g* factor, and two other instances in which this difficulty of evaluation is circumvented to some extent through application of information additional to wave numbers of spectral transitions, as a direct application of computational spectrometry.

6. GALLIUM HYDRIDE, GaH

Gallium hydride is an esoteric and obscure chemical compound, of no particular technical significance; through infrared spectra, its vapour nevertheless proves useful for elucidation of diatomic molecular properties in an exemplary manner. Although vibration-rotational spectra but no pure rotational spectra of gallium hydride have been measured, 1094 lines in this data set comprise an especially useful collection because spectra, from experiments entailing absorption [91,92] or emission [93] of radiation in the mid infrared region, of four isotopic variants – $^{69}Ga^{1}H$, $^{71}Ga^{1}H$, $^{69}Ga^{2}H$ and $^{71}Ga^{2}H$ – involve vibration-rotational energies over almost the same range, corresponding to $v=5$ maximum for GaH and $v=7$ maximum for GaD. Reduction of all data from emission spectra [93] with unduplicated data for GaH in absorption [91] according to the Dunham approach with Radiatom yields evaluated parameters according to results presented in Table 1.

Each stated uncertainty in this and other tables represents one estimated standard error, propagated to parameters from uncertainties of measurements of wave numbers; the uncertainties of the latter measurements were provided by authors of papers [91,93] reporting those data, and the weight of each datum in the non-linear regression was taken as the reciprocal square of those uncertainties. As the reduced standard deviation of the fit was 0.92, so less than unity, the authors

Table 1. Coefficients of radial functions and other molecular parameters of GaH X $^1\Sigma^+$

c_0/m^{-1}	10463962 ± 22	s_0^{Ga}	0.696 ± 0.066
c_1	-1.3474749 ± 0.0000078	t_0^{Ga}	-3.38 ± 0.33
c_2	1.038431 ± 0.000030	t_1^{Ga}	5.33 ± 0.65
c_3	-0.521864 ± 0.000111	t_0^{H}	-3.16990 ± 0.00060
c_4	0.04433 ± 0.00054	t_1^{H}	7.3384 ± 0.0167
c_5	-0.1159 ± 0.0026	t_2^{H}	-14.82 ± 0.26
c_6	0.2471 ± 0.0067	t_3^{H}	16.19 ± 0.42
c_7	-0.0182 ± 0.031	$u_1^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	-10.80866 ± 0.00105
c_8	-1.688 ± 0.106	$u_3^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	29.71 ± 0.86
		$u_4^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	-66.4 ± 3.8
		$u_5^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	127.6 ± 10.9
		$u_6^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	-223 ± 27
$U_{0,1}/\mathrm{m}^{-1}\ \mathrm{u}$	611.64646 ± 0.00163		
$U_{1,0}/\mathrm{m}^{-1}\ \mathrm{u}^{1/2}$	159996.185 ± 0.044		
$R_e/10^{-10}\ \mathrm{m}$	1.6601526 ± 0.0000022		
$k_e/\mathrm{N\ m}^{-1}$	150.823636 ± 0.000084		

likely expressed those uncertainties slightly conservatively, but clearly an application of Dunham's formalism embedded in computer programme Radiatom provides a satisfactory reduction of these data. Parameters in the left column pertain to mechanical effects, according to Dunham's term [5], and in the right column to extra-mechanical effects. Only ten parameters in the left column are independent: those explicitly fitted include c_j with $1 \leq j \leq 8$, $U_{1,0}$ and $U_{0,1}$; parameters c_j are coefficients in $\mathrm{V}(z)$ according to formulae 21 and 52, and two others are defined in terms of the corresponding Dunham coefficients through formulae 13. The leading coefficient c_0 for potential energy is defined as

$$c_0 = U_{1,0}^2/(4U_{0,1}) \tag{63}$$

thus maintaining its rigorous independence of atomic mass; the equilibrium force coefficient k_e, pertaining to Hooke's law in the limit of an harmonic oscillator, is related to $U_{1,0}$ through

$$k_\mathrm{e} = (2\pi c U_{1,0})^2/(10^3 N_\mathrm{A}) \tag{64}$$

whereas the equilibrium internuclear separation R_e is related to $U_{0,1}$ through

$$R_\mathrm{e}[10^3 N_\mathrm{A} h/(8\pi^2 c U_{0,1})]^{1/2} \tag{65}$$

A factor Avogadro's constant multiplied by 10^3 enters these expressions on condition that atomic and electronic masses be expressed, as is customary in spectral analyses, in unified atomic mass unit; both $U_{1,0}$ and $U_{0,1}$ contain mass in their units, despite their values being formally independent of atomic mass. The standard errors associated with values of k_e and R_e in Table 1 include contributions from errors of pertinent fundamental physical constants [94].

Of values in the right column of Table 1, the specified parameters are coefficients of z in formulae 45, 46 and 47, pertaining to vibrational and rotational g factors and adiabatic corrections respectively, with atomic centres $\mathrm{B}=\mathrm{Ga}$ and $\mathrm{A}=\mathrm{H}$ for this particular compound. Apart from the value of u_2^H that was constrained to zero in the ultimate fit because preliminary fits indicated that its standard error much exceeded its magnitude, values of other parameters beyond c_8, s_0^Ga, t_1^Ga, t_3^H and u_6^H in their respective series, and also all u_j^Ga and s_j^H, are not assumed to be zero, but are simply indeterminate from available spectral data within the chosen model, as explained above. Although it is absolutely inappropriate to constrain to zero the value of a particular parameter within a selected set of parameters c_j, even though an estimated standard error of that parameter considered for rejection be larger than its magnitude, it is appropriate, if warranted on an objective basis of statistical criteria, to constrain to zero value a particular parameter within a selected set s_j, t_j or u_j, as is practised with u_2^H in this case; a crucial distinction between these methods of handling parameters arises because c_j occur non-linearly in expressions both Y_kl and Z_kl – see formula 48 for instance, whereas the latter parameters for extra-mechanical effects occur only linearly in expressions for Z_kl – compare formula 49. In our original report [89], we employed parameters in not quite the same set; the set here takes account of the fact that adiabatic corrections, reflected by coefficients of type u_j, are expected to be more important for a light species such as H than the effect of the vibrational g factor, reflected in coefficients of type s_j, and vice versa for a massive species such as Ga, on a basis of calculations of adiabatic corrections [87] discussed above and our accumulated experience with rotational and vibrational g factors. The latter supposition is subject to verification when calculations of adiabatic corrections for GaH become practicable. Parameters in a set selected for this fit thus reflect arbitrary selection to some extent; of parameters in all various sets that were tested, this set in Table 1 produced the smallest reduced standard deviation of fit. Although parameters in an alternative set might produce an even smaller standard deviation, if such a set were to include parameters that arise in higher orders of perturbation theory to the exclusion of parameters in lower orders, such a set would be clearly illegitimate.

Before drawing deductions about molecular properties from results in Table 1, we consider further statistical aspects. The program Radiatom produces not only estimated standard errors of parameters, such as those presented in Table 1, that derive from variances, but also their coefficients of correlation ρ_{jk} from a corresponding covariance matrix. For GaH and results appearing in Table 1, there are 22 adjustable parameters: hence a symmetric matrix of these coefficients contains 231 distinct entries; numerical magnitudes of only 19 exceed 0.9. Such a proportion of magnitudes greater than 0.9 is a typical occurrence in fits of real positive numbers to polynomials that are not orthogonal. Magnitudes of correlation coefficients near unity derived from the covariance matrix pose no problem for numerical stability in Radiatom because it operates with nominal precision 32 decimal digits. For GaH, 14 values with $|\rho| > 0.9$ occur between coefficients u_j^H, as expected because these coefficients have mostly no counterparts t_j^H that arise in the same orders of perturbation theory. Of other magnitudes near unity, between t_0^{Ga} and $U_{0,1}$ the value of ρ is -0.997, which is still not the largest magnitude off the diagonal of this correlation matrix; such a large magnitude is reasonable because the difference of reduced mass between $^{69}Ga^1H$ and $^{71}Ga^1H$ is minute. Likewise a value of ρ connecting s_0^{Ga} and $U_{1,0}$ is -0.95. In contrast only one moderate magnitude of ρ connects t_0^H with another parameter, specifically t_1^H; the value is -0.82, whereas for u_1^H the largest magnitude of ρ to another parameter is less that 0.28 – entirely innocent; these results reflect the large difference of reduced mass between Ga^1H and Ga^2H, and hence a large sensitivity of values of extra-mechanical parameters for H to moderately precise spectral data. A claim [90] that coefficients u_1^a and t_0^a are necessarily highly correlated is hereby refuted; such correlation is broken as explained above. To indicate a context for these values, the value of ρ between c_1 and c_2 is -0.87, not for only GaH but typically also for other molecular species, again characteristic of fits to non-orthogonal polynomials. On a basis of both standard errors and correlation coefficients, coefficients $t_0^H = -3.16990 \pm 0.00060$ and $u_1^H / 10^6\ \mathrm{m}^{-1} = -10.80866 \pm 0.00105$ are hence clearly statistically well defined, whereas $t_0^{Ga} = -3.38 \pm 0.33$ and $s_0^{Ga} = 0.696 \pm 0.066$ are poorly defined despite ratios of their magnitudes to respective standard errors exceeding 10.

Production of an acceptable value of reduced standard deviation of a fit required multiple parameters u_j^H, up to $j = 6$. Values of these parameters with $j > 2$ likely reflect not only adiabatic corrections; their association with a particular term in the effective hamiltonian is hence questionable. From both a point of view of partition of effects among parameters s_j, t_j and u_j in an incomplete subset for a particular range of Z_{kl}, as discussed above, and from particular statistical considerations, however, parameters t_0^H and u_1^H can be confidently attributed to pertain practically exclusively to the rotational *g* factor and to adiabatic corrections, respectively.

On this basis we proceed to deduce, from pertinent radial coefficients in table 1, values of molecular properties, within a quasi-physical model consistent with an effective hamiltonian of form in formula 29. The equilibrium internuclear distance is purportedly a measure of the length of the chemical bond between atomic centres Ga and H; for this highly precise value of R_e in table 1 the relative error is about one part per million, and the absolute error is about one tenth of a typical nuclear radius. Evidently just as precisely evaluated, the equilibrium force coefficient k_e has a value about a quarter of that typical of hydrides such as CH and NH with 'single' chemical bonds, consistent with GaH having a thermochemical dissociation energy smaller than that of these other specified hydrides [95] and with a general decrease of such force coefficients with atomic centres involving chemical elements beyond the row in the periodic chart containing Li and Ne. The radial function V(z) for potential energy has a maximum range of validity $1.3 \leq R/10^{-10}\ \mathrm{m} \leq 2.4$, consistent with the classical turning points for vibrational state $v = 5$ of GaH. Coefficients c_j up to $j = 8$ imply expressions Y_{kl}^i up to $Y_{5,0}$, $Y_{4,2}, \ldots, Y_{0,10}$, in total 36 applicable to each isotopic variant, hence 144 numerical values of coefficients in formula 27 that, with corresponding numerical values for Z_{kl}^i derived from other radial coefficients in the right column of table 1, not only reproduce the measured wave numbers of 1094 spectral lines within their precision, on average, but also predict accurately the wave numbers of unmeasured transitions within the same range of v and J; less accurate prediction moderately beyond that range is likely also practicable. The radial functions pertaining to extra-mechanical effects have smaller ranges of validity because they are evaluated to lesser degrees of polynomials in z and because they likely contain mixed effects of $g_v(z)$, $g_r(z)$ and $V'(z)$, apart from contamination from $V''(z)$ that is unlikely to be significant.

Upon inverting formulae 59 and 60, we obtain these relations [89],

$$p_0 = 1/2\, eR_e(t_0^{Ga} - t_0^H) \tag{66}$$

$$g_r(R_e) = m_p(t_0^H/M_H + t_0^{Ga}/M_{Ga}) \tag{67}$$

by means of which we estimate values of electric dipolar moment and rotational *g* factor of ^{69}Ga^{1}H at R_e. From formula 66, the value $(2.8 \pm 4.4) \times 10^{-30}$ C m is clearly insignificant, indicating neither magnitude nor sign of p_0 relative to the molecular axis, because, according to table 1, even the nominal error of t_0^{Ga} is larger than the difference between t_0^{Ga} and t_0^H. In contrast, through formula 67 the rotational *g* factor of ^{69}Ga^{1}H at R_e is highly significantly evaluated, -3.1188 ± 0.0049, because t_0^{Ga} and its error are divided by a large atomic mass. Apart from a negative sign, the latter value has a large magnitude, relative to those of HI, HBr

HCl and HF [56] with increasing values in a range [0.10, 0.45] respectively; a negative sign and large magnitudes are common to other hydrides of group 13, for which calculations yield values −8.207 for $^{11}B^{1}H$ [96] and −3.370 for $^{27}Al^{1}H$ [97]. Calculations [98] of $g_r(R_e)$ for $^{69}Ga^{1}H$ yield values in a range [−2.9457, −3.4440] depending on a level of sophistication of computations of molecular electronic structure. Upon inverting formulae 58 and 59, we obtain relations [66] analogous to those above,

$$p_1 = 1/2\ eR_e(s_0^{Ga} - s_0^{H}) \tag{68}$$

$$g_v(R_e) = m_p(s_0^{H}/M_H + s_0^{Ga}/M_{Ga}) \tag{69}$$

but these are inapplicable in the present circumstances to deduce a value of the vibrational g factor for GaH because we lack an estimate of s_0^{H}. By means of further relations [66],

$$p_1 - p_0 = 1/2\ eR_e(t_1^{Ga} - t_1^{H}) \tag{70}$$

$$dg_r(z)/dz_{|R_e} = m_p(t_1^{H}/M_H + t_1^{Ga}/M_{Ga}) \tag{71}$$

we might apply the latter to estimate the derivative of rotational g factor of $^{69}Ga^{1}H$ at R_e to be 7.412 ± 0.019, but the former relation can yield only a rough estimate $(-2.67 \pm 0.86) \times 10^{-29}$ C m of a difference between coefficients p_1 and p_0 in a radial function, formula 56, for electric dipolar moment because p_0 is indeterminate from present spectral data of GaH. We might nevertheless infer that the permanent electric dipolar moment of GaH is likely to be small, but its derivative at R_e likely large; these conditions are reminiscent of similar characteristics of CO [99] and NO [100], for which a small permanent electric dipolar moment occurs and for which the polarity of the radial function alters near the equilibrium distance. Because these differences between radial coefficients s_j and t_j occur in formulae such as 66, 68 and 70, we concur with a suggestion [90] that electric dipolar moments obtained from spectra of samples in absence of electric or magnetic field might be difficult to evaluate or unreliable from only moderately precise spectral data, but the situation is clearly different for at least the rotational g factor of GaH.

We compare results of the present treatment of GaH with those published elsewhere. From measurements of absorption spectra of $^{69}Ga^{1}H$ and $^{71}Ga^{1}H$ [91], parameters of type A_{kl} were evaluated for separate isotopic variants. After further measurements of also $^{69}Ga^{2}H$ and $^{71}Ga^{2}H$, parameters of type A_{kl} for the latter species and of types B_{kl} and Δ_{kl} common to all four variants were reported [92]. Our first analysis [101] of spectra of GaH was based on only absorption spectra, 208 lines reported in two papers [91,92]; although it resulted in evaluation of parameters of essentially empirical radial functions, similar to $V(z)$, $V'(z)$ and $g_r(z)$ in formula 29, the treatment was hampered by both paucity of data and incompletely developed theory. After publication of data from emission spectra [93], a subsequent reanalysis [89] demonstrated the possibility of evaluation of molecular electric and magnetic properties from analysis of vibration-rotational spectral data of samples measured without applied fields, but again the treatment suffered from lack of a theoretical basis that became available subsequently [66]. Comparison of our present results with those from only emission spectra [93] sheds light on several aspects of the present discussion. From spectra that included 1045 lines (omitting previously reported lines [91,92]) in sequences with $\Delta v = 1$ up to $v = 4$ for GaH and $v = 7$ for GaD, a fit of these data yielded freely adjustable parameters A_{kl} in formula 2 for each of four isotopic variants; these parameters numbered 70 in total. Combining data for all four species yielded first 19 unconstrained parameters B_{kl}, defined above in relation to formula 19, with 11 further parameters $\Delta_{\mathrm{kl}}^{\mathrm{Ga,H}}$; in a further stage, ten constrained parameters $U_{\mathrm{k,0}}$ and $U_{\mathrm{k,1}}$ were evaluated that imply a further 25 parameters U_{kl} with $l > 1$, also with 11 further parameters $\Delta_{\mathrm{kl}}^{\mathrm{Ga,H}}$. The final stage of data reduction involved numerical solution of Schrodinger's equation, 1045 times per iteration for several iterations, in which a radial function for potential energy is based on that of Morse [102] but with a polynomial in argument $\frac{1}{2}z$ in the exponent, accompanying expansions in displacement $(R - R_e)$ corresponding roughly to $\mathrm{V}'(R)$ and $\mathrm{g_r}(R) m_e/m_p$ in formula 29. (That numerical approach is incapable of handling directly another radial function $\mathrm{g_v}(R)$ in formula 29.) In contrast, according to Dunham's symbolic approach, to obtain the general exact algebraic expressions one solves Schrodinger's equation once [30], or equally well applies matrix mechanics [31] or other methods [26], because those expressions are independent of a correct method of their production; only simple substitution at arbitrarily selected precision is required thereafter to evaluate Dunham coefficients Y_{kl} during fits of data, and therefrom the wave numbers of transitions according to formula 54. That reduction [93] resulted in values of R_e and 27 coefficients, each presented with 16 decimal digits, of radial functions – $10\beta_j$ in the exponent, four coefficients for Ga and eight for H in functions corresponding to those in formula 47 but with displacement as argument, and five coefficients for only H in an expansion resembling one of those in formula 46, also in terms of displacement; hence these authors used disparate variables related to distance within the same fit. Although their expansions of fourth and ninth orders similar to formula 47 clearly pertain primarily to adiabatic corrections, Campbell et alii [93] attribute these to "Born-Oppenheimer breakdown and homogeneous nonadiabatic mixing"; the latter, actually associated with the vibrational g factor, enters also into values of their parameters for their other radial functions with argument displacement, as described above. Whereas to fit 1094 data in table 1 we evaluate five parameters of type u_j^{H}, that alternative approach [93] required a polynomial of ninth order to fit 1045 data over a smaller range of wave number $\tilde{\nu}$, or vibrational quantum number v, for GaH.

Even for potential energy the other approach [93] required one parameter additional to ours, apart from $\mathcal{D}_e$; the latter quantity, equilibrium binding energy, is stated to be based on "thermochemical" data, but the cited source [95] indicates a value of dissociation energy $\mathcal{D}_0$ "<2.84 eV" to arise from spectral analysis. Such an upper limit must be understood to provide an asymptotic limit for $\mathrm{V}(R)$ at large R in a formula of Morse type because an attempted evaluation of $\mathcal{D}_e$ from only infrared spectral data is unreliable. The stated reason for the choice of such a fitting form is to generate "a reliable internuclear potential-energy function…to obtain information on the high-lying v, J levels" [93]. If "a reliable…function" be supposed to imply accurately predictable wave numbers of transitions involving such states, how reliable such information might be is questionable at best because the value of $\mathcal{D}_e$ is specified [93] as "2.29×10^4 cm^{-1}", without acknowledging that it is an upper limit, with precision implied to be 8100 m^{-1} at best; as the best precision of measured wave numbers of GaH is ~0.02 m^{-1} [93], the ratio of these values is ~400000. In any case there exists an atomic isotopic effect such that the energy of separate Ga and H atoms differs from that of separate Ga and D atoms, reflected in distinct values of $\mathcal{D}_e$, by ~300 m^{-1}, likewise much greater than the precision of measured infrared spectral lines. The known vibrational states occupy only the lowest third of that range of potential energy below the maximum value of the supposed dissociation limit; the error implied by an uncertainty in $\mathcal{D}_e$ would be comparable with the vibrational spacing of GaD at a moderate value of quantum number v, much less than a value $v_D \sim 40$ expected just below the dissociation limit. That function for potential energy of modified Morse form [93] might appear superficially to possess a qualitatively appropriate shape, although it is obviously not correct because limiting behaviour at large R must conform to an inverse power of R rather than an exponential approach to an asymptotic limit; as a possibility of a maximum in that function or other effect of significant interaction with electronically excited states can not be excluded, the selected form is entirely speculative. Any justification of a radial function for potential energy of that chosen form is clearly spurious. The polynomial of ninth degree for extra-mechanical effects diverges rapidly on either side of the defined range, further contributing to massive deterioration of accuracy of predictions of wave numbers of transitions even modestly beyond the range of vibrational states included in that analysis [93], even if the function for potential energy might be reliable beyond that range. From a statistical point of view, in lack of an exact theoretical model – which exists for neither potential energy nor auxiliary radial functions, an objective of predicting accurately the wave numbers of transitions involving vibration-rotational states with large values of quantum numbers v and J is unattainable, because gross extrapolation, based on increasingly inaccurate data as v increases to 4 for GaH or 7 for GaD, would be required, even with an exactly defined asymptotic limiting value of $V(R)$ at large R. Although the nature of reduced displacement variable z allows limiting conditions [103] to be applied to $V(z)$ at both $R=0$ for the united atom and $R \to \infty$ for the separate atoms, unlike Dunham's function $V(x)$, these conditions have never been applied systematically because consideration of the underlying physical implications signifies that such application would not be sensible.

Parameter R_e is no physical observable, merely a fitting parameter like any other, even though it represents a special point on a curve of $V(R)$ that is likewise no physical observable. Jones and coworkers reported no value of R_e; their value (611.6337 ± 0.0045) m^{-1} u [92] of "$U_{0,1}$" (actually $B_{0,1}$) implies $R_e/10^{-10}$ m $= 1.6601699 \pm 0.0000061$, which differs inappreciably from a corresponding value in table 1. Because we take into account practically all factors that influence the value of R_e, the latter value is highly accurate, within its stated uncertainty, not merely precise and prone to systematic error. That tabulated value of R_e is larger than that reported by Bernath and coworkers [93] by ~ 47 of their standard errors, which take no account of uncertainty of fundamental physical constants; the reason for their value being smaller is clearly the failure to include in their fit any parameter related to the rotational g factor, which consequently causes that systematic deviation. The results present in table 1 differ little from those published [89] after appearance of data from emission spectra [93], but for these data of GaH even the latter results [89] demonstrate unequivocally the superiority of the application of a method of reduction of diatomic molecular spectra of GaH based systematically on Dunham's algebraic approach over an approach based on purely numerical procedures [93]: more numerous data are reproduced accurately with fewer parameters, and at least one such parameter t_0^{H} embodies physical significance beyond an arbitrarily selected approximate model because it predicts accurately the result [98] of a prospective experiment based on the Zeeman effect [56].

The quality and consistency of 1094 data for GaH in a set of which reduction with computer programme Radiatom yields parameters present in table 1 invite a more general numerical test of Dunham's theory. A question might arise about an ability to represent rotational effects based on vibrational information. For instance, coefficient a_6 in $\mathrm{V}(x)$, formula 16, or c_6 in $\mathrm{V}(z)$, formula 52, occurs first in Dunham coefficients $Y_{4,0}$ for pure vibrational effects and $Y_{0,8}$ for pure rotational effects, apart from $Y_{3,2}$, $Y_{2,4}$ and $Y_{1,6}$ for vibration-rotational effects. As parameters c_{j}, $1 \leq j \leq 6$, in table 1 are well defined statistically, one clearly expects both $Y_{4,0}$ and $Y_{0,8}$ to be correspondingly well defined, despite the disparity in their magnitudes: for $^{69}\mathrm{Ga}^{1}\mathrm{H}$, $Y_{4,0} = -0.6111704\ \mathrm{m}^{-1}$ and $Y_{0,8} = -8.447813 \times 10^{-28}\ \mathrm{m}^{-1}$. Even when the latter quantity be multiplied by $[J(J+1)]^8$ for $J = 29$ – the largest value in measured spectra [91,93], the product is only $-2.8 \times 10^{-4}\ \mathrm{m}^{-1}$, much smaller than the precision, $\geq 0.06\ \mathrm{m}^{-1}$, of measurement of wave numbers of transitions. A fit of spectral data to fitting coefficients A_{kl} is thus unlikely to yield directly a significant value of $A_{0,8}$, but a value of $Y_{0,8}$ derived consistently, even though indirectly from the same spectral data through other parameters such as a_{j} or c_{j}, is attained with great significance. We tested the sensitivity of rotational contributions to vibrational data by greatly diminishing the weight of the wave number of each transition in the data set with $J > 5$; although such transitions remain within the data set so that calculated and measured wave numbers become directly compared in the output from a fit, that fit becomes entirely insensitive to corresponding measured wave numbers of these transitions. With parameters in the same set as in table 1, the results of this fit demonstrate only a slightly degraded quality of fit, reflecting the effectively decreased number of fitted data, and calculated wave numbers of transitions with altered weights differ almost negligibly from those in other fits with standard weights. Hence Dunham's approach that involves taking into account rotational effects through expansion of $B_{\mathrm{e}}/(1+x)^2$ in the effective potential energy [5] is entirely justified. Provided that additional terms in an effective hamiltonian for non-mechanical effects – those in formula 29, except $\mathrm{V}''(R)$, beyond those in formula 14 – are properly taken into account, Dunham's theory provides a sufficient and complete description of regular molecular spectra – those free of heterogeneous perturbations, as is typically the case for diatomic molecular species within their electronic ground states.

7. DIHYDROGEN, H_2

A diatomic molecule for which atomic numbers of both atomic centres are the same – $Z_a = Z_b$ – but for which masses M_a and M_b of separate atoms A and B might differ poses advantages for testing theories. For instance instead of parameters for extra-mechanical effects in two sets when $Z_a \neq Z_b$ – one for each of two atomic types, there is only one set, and a molecular reduced mass is applicable instead of individual atomic masses of separate atoms; compare formulae 33, 34 and 35 with their counterparts 37, 38 and 31, for instance. Precisely measured spectra of such elemental molecular species are rare: of chemically stable and gaseous diatomic species near 300 K, only H_2, N_2, O_2 and three dihalogen species are readily available; many other diatomic elemental species formed at elevated temperatures above solid elements have electronic ground states for which spin and orbital angular momentum complicate the spectra. Of those six, F_2, which is highly reactive in any case, lacks any practical isotopic variants, and O_2 has an electronic ground state X $^3\Sigma_g^-$ with accompanying complications from net electronic angular momentum and its coupling with rotational angular momentum; some application of Dunham theory has nevertheless been made to O_2 [104]. Although for N_2 there are fairly precise measurements of coherent Raman spectra [105], the extra-mechanical effects are small and poorly defined. For all six specified gaseous homonuclear species plus I_2, electronic spectra have been measured with attendant vibrational and rotational structures, but the precision of those measurements is generally much smaller than for typical contemporary vibration-rotational spectra of heteronuclear molecules in infrared absorption or emission, and a direct involvement of excited electronic states within a particular spectral analysis introduces correlations between parameters for these combining states. The problem arises from the fact that infrared spectra of homonuclear diatomic molecules in the gaseous phase corresponding to vibration-rotational transitions in absorption or emission are extremely weak, relying on magnetic dipolar or electric quadrupolar transition moments for their observed intensity; an alternative technique, Raman scattering, applied to transitions other than pure rotational and fundamental vibration-rotational bands yields only exceedingly weak signals.

Hydrogen is the most abundant chemical element in the universe, and in its various atomic and molecular forms furnishes a sensitive test of all of experimental, theoretical and computational methods. Vibration-rotational spectra of dihydrogen in six isotopic variants constituting all binary combinations of H, D and T have nevertheless been recorded in Raman scattering, in either spontaneous or coherent processes, and spectra of HD have been recorded in absorption. Despite the widely variable precision of these measurements, the quality of some data for small values of vibrational quantum number is still superior to that of data from electronic spectra [106], almost necessarily measured in the ultraviolet region with its concomitant large widths of spectral lines. After collecting 420 measurements of wave numbers of lines reported in 32 papers originating in 16 laboratories, we analysed [107,108] these spectral data with Radiatom and Radiatom II; we rejected 30 data that are severely discordant with remaining data, reflecting poor calibration or blunder of measurement. To avoid arbitrary exclusion of some data in favour of other, we retained among accepted data duplicate measurements of some transitions from separate laboratories, but all data were carefully weighted to reflect their varied precision. In view of data of such questionable quality, one can clearly not contemplate attempting to evaluate directly molecular parameters related to extra-mechanical effects without additional information. As a dihydrogen molecule contains only two electrons, calculations of molecular electronic structure and properties based on that structure are eminently practicable. Kolos and Wolniewicz calculated adiabatic corrections [110,111], and according to methods [56] developed for other diatomic and triatomic molecular species such as those already cited [96,97,98] we made new calculations of the rotational and vibrational g factors as a function of internuclear distance over a large range.

Fitting calculated results of $g_r(R)$ to a polynomial in z, we imposed coefficients t_j thereof as constraints in a separate fit of 390 accepted spectral data to evaluate R_e and coefficients c_j, s_j and u_j. Those values of coefficients t_j appear within brackets in a column headed 'fit T' in table 2 with standard errors of that fit to a polynomial; standard errors of other parameters in that column reflect results of the fit with Radiatom. On a basis of this fit we were able to predict a value $g_v(R_e) = 0.3136 \pm 0.0046$ of the vibrational g factor for $^1H_2$. Although this value differs from a value $g_v(R_e) = 0.2325$ from subsequent calculations [107], the experimental estimate is still much smaller than a similarly calculated rotational g factor, $g_r(R_e) = 0.8908$ [56], that agrees almost exactly with direct experimental measurement [112]. To confirm the stability of our approach to fitting spectra, we undertook a separate fit, in this case employing adiabatic corrections as constraints, to evaluate R_e and radial coefficients c_j, s_j and t_j. In the results in table 2, column 'fit U', the values of u_j fitted in a polynomial in z to computational data for adiabatic corrections [110,111] appear within brackets, with other radial coefficients and their standard errors from a fit of the same 390 spectral data. We consequently derive another estimate of the vibrational g factor, $g_v(R_e) = 0.2800 \pm 0.0086$ for $^1H_2$, which is smaller than the other value deduced from spectra but still larger than the calculated value. Fitted values of t_0 and t_1 in column 'fit U' are near the corresponding calculated values in column 'fit T'; conversely, fitted values of u_1 and u_2 in column 'fit U' are near the corresponding calculated values in column 'fit T'. Further fitted parameters s_j, t_j and u_j for extra-mechanical effects reflect the rough data, indicated by the reduced standard deviation of either fit being $\hat{\sigma} = 1.46$, significantly greater than unity; inconsistencies among 390 retained data from diverse sources, apart from gross discordance that required 30 other data to be rejected, are responsible for this condition, and emphasize the need for a thorough experimental remeasurement of spectra for pure rotational and vibration-rotational transitions of H_2 in its several isotopic variants, preferably extending the range of vibrational and rotational states sampled in transitions. Other parameters pertaining to potential energy $V(z)$ have comparable values between the two fits, as they are less sensitive to

Table 2. Coefficients of radial functions and other molecular parameters of H_2 X $^1\Sigma_g^+$ or $^1\Sigma^+$

	Fit T	Fit U
c_0/m^{-1}	7970836.8 ± 79	7970784.5 ± 77
c_1	-0.604167 ± 0.000118	-0.603753 ± 0.000135
c_2	0.21030 ± 0.00024	0.20973 ± 0.00033
c_3	-0.14441 ± 0.00187	-0.14889 ± 0.00186
c_4	0.01276 ± 0.0025	0.02164 ± 0.0026
c_5	-0.1404 ± 0.0085	-0.1308 ± 0.0086
c_6	0.1973 ± 0.0102	0.1737 ± 0.0100
c_7	-0.0524 ± 0.0106	-0.0614 ± 0.0109
c_8	-0.0737 ± 0.0178	-0.0459 ± 0.0173
c_9	0.0880 ± 0.0092	0.0694 ± 0.0082
c_{10}	-0.1074 ± 0.0172	-0.1055 ± 0.0169
s_0	0.1569 ± 0.0023	0.1301 ± 0.0043
s_1	[0]	-0.528 ± 0.026
s_2	[0]	[0]
s_3	6.69 ± 0.69	9.59 ± 0.83
t_0	$[0.44562 \pm 0.00044]$	0.4523 ± 0.0030
t_1	$[-0.09858 \pm 0.0025]$	-0.0836 ± 0.0174
t_2	$[-0.09558 \pm 0.0066]$	-0.603 ± 0.108
t_3	$[-0.09219 \pm 0.021]$	…
t_4	$[-0.1354 \pm 0.0140]$	…
t_5	$[-0.0468 \pm 0.043]$	…
t_6	$[0.4275 \pm 0.027]$	…
$u_0/10^6\ \mathrm{m}^{-1}$	…	$[10.52472 \pm 0.00072]$
$u_1/10^6\ \mathrm{m}^{-1}$	-4.025 ± 0.024	$[-4.0384 \pm 0.0049]$
$u_2/10^6\ \mathrm{m}^{-1}$	2.007 ± 0.061	$[2.1451 \pm 0.0197]$
$u_3/10^6\ \mathrm{m}^{-1}$	[0]	$[1.728 \pm 0.033]$
$u_4/10^6\ \mathrm{m}^{-1}$	2.75 ± 0.23	$[1.384 \pm 0.086]$
$u_5/10^6\ \mathrm{m}^{-1}$	…	$[0.353 \pm 0.053]$
$u_6/10^6\ \mathrm{m}^{-1}$	…	$[-0.727 \pm 0.109]$
$U_{0,1}/\mathrm{m}^{-1}\ \mathrm{u}$	3066.7339 ± 0.0110	3066.7074 ± 0.0124
$U_{1,0}/\mathrm{m}^{-1}\ \mathrm{u}^{1/2}$	312694.3 ± 2.1	312691.95 ± 2.15
$R_e/10^{-10}\ \mathrm{m}$	$0.74141301 \pm 0.00000133$	$0.74141620 \pm 0.00000150$
$k_e/\mathrm{N\ m}^{-1}$	576.0898 ± 0.0078	576.0810 ± 0.0079

irregularities in the data. From table 2, the mean value of equilibrium internuclear distance, $R_e/10^{-10}\ \mathrm{m} = 0.7414146 \pm 0.0000020$, from experiment agrees satisfactorily with, but is likely more accurate than, the calculated value 0.74143×10^{-10} m [110] (with a current value of Bohr radius [94]), if these quantities be accorded their conventional meanings. Our experimental value formally takes into account all extra-mechanical terms in formula 29, except those in $V''(z)$, that might affect the value of R_e at a level of order 10^{-16} m, which is comparable with experimental error 2×10^{-16} m of this quantity propagated from measurements of wave numbers of transitions; in contrast the effect of the rotational g factor on the value of R_e occurs at a level of order 5×10^{-14} m.

Each radial function – $\mathrm{V}(z)$, $\mathrm{g_v}(z)$, $\mathrm{g_r}(z)$ and $\mathrm{V}'(z)$ – of which coefficients of z are evaluated from spectral data has a maximum range of validity, depending on the quality and quantity of spectral data for isotopic variants, and expressible in terms of a range of quantum numbers of vibration-rotational states, or spectral term E_{vJ}, or range of internuclear distance. For $\mathrm{V}'(z)$ and $\mathrm{g_r}(z)$ the latter range of $R/10^{-10}$ m is [0.53, 1.05], corresponding to classical turning points of $V(R)$ for $v \sim 2$ for $^1\mathrm{H}_2$; although spectral data for isotopic species are available for greater energies, their quality precludes reliability over a greater range. Because acceptable data for H_2 are available up to $v=5$ and for HD to $v=6$, or $E \sim 2.1 \times 10^6$ m^{-1} in either case, for $\mathrm{V}(z)$ the corresponding range of $R/10^{-10}$ m is larger, [0.47, 2.05]. For $\mathrm{g_v}(z)$, because of the disparity of results between fits T and U, from experiment a mean value $g_{\mathrm{v}} \sim 0.3$ would be applicable near R_{e}; further coefficients s_1 and s_3 from either fit lack other than nominal numerical significance for reasons mentioned above. Plots of curves of any radial function derived from experiment are impracticable without an assumption that further, and unevaluated, radial coefficients have explicit numerical values, zero or otherwise, which is unwarranted according to application of Dunham's formalism to spectral analysis. From computations of molecular electronic structure, values of $\mathrm{g_r}$ and g_{v} as a function of internuclear distance over a broad range, and discussion of their features, are presented elsewhere [107].

There exists no significant comprehensive fit of spectral data of H_2 with which we might here make comparison. Our discussion above demonstrates that, as for GaH above, application of an algorithm based on Dunham's algebraic approach to analysis of vibration-rotational spectral data of H_2, especially through implementation of hypervirial perturbation theory [30,72] that allows the term for the vibrational g factor in the hamiltonian in formula 29 to be treated directly in that form, proves extremely powerful to derive values of fitting parameters that not only have intrinsic value in reproducing experimental data of wave numbers of transitions but also relate to other theoretical and experimental quantities.

8. LITHIUM HYDRIDE, LIH

The only other diatomic molecular species for which calculations of the radial dependence of adiabatic corrections, rotational and vibrational g factors are available is LiH. Although at 300 K this compound is a crystalline solid substance with a structure of KCl type, at temperatures above its standard melting point 951 K the vapour contains polar diatomic molecules of stoichiometry according to its formula, as well as dimers and molecular clusters in variable proportions; spectral measurements on this vapour in absorption or emission have hence yielded data on not only wave numbers of pure rotational and vibration-rotational transitions, among others, of these diatomic molecules but also information on their electric and magnetic properties through applications of Zeeman and Stark effects respectively in appropriate experiments. Like H_2, lithium hydride is amenable to practice of calculations of molecular electronic structure for internuclear distance over a broad range because a molecule contains only two light atomic nuclei and four electrons; relativistic effects, which accurate calculations must take into account but which do not directly enter analysis of experimental data, on differences of molecular energies are therefore negligible, like radiative effects [113], at a level pertinent to typical spectra at moderately great resolution, although they both become important for calculations on LiH at a level of spectral resolution at which effects of $V''(z)$ must be considered. Ignoring effects of nuclear volume or field shifts, we require seven radial functions, with their corresponding parameters, for direct fitting of spectra of LiH – potential energy, and contributions to adiabatic corrections, rotational and vibrational g factors for atomic centres of each type, according to formulae 52, 47, 45 and 46 respectively. We expect contributions to total $Y_{kl}+Z_{kl}$ from each of the latter three effects to have comparable magnitudes, but smaller than a dominant contribution from potential energy by a factor a ratio of electronic and protonic rest masses, m_e/m_p, or less.

This species LiH was the first for which, by way of interactive computational spectrometry, we combined experimental data and results of calculations of molecular electronic structure to make a global fit [114] of wave numbers of transitions from available infrared and microwave spectra. The basis of that procedure was that, in principle, measurements of the rotational g factor for vibration-rotational states with v and J over a large range would allow one to calculate the radial function $g_r(R)$; as measurements of g_r of $^7Li^1H$ and $^7Li^2H$ are available for only $v=0$ and $J=1$ [115], with the rotational dependence of g_r roughly estimated [116], we simulated prospective results from further such experiments through those computations. Repeating this strategy with improved calculations [107,109], we fitted available spectra to obtain results presented in table 3; as for H_2 in table 2 and fit T, 17 values of $t_j^{Li,H}$, reported within brackets with their standard errors, result from fitting computed results for $g_r(R)$ and $p(R)$ to a polynomial in z for each value of internuclear distance, based on use of formulae 59 and 60 with R instead of R_e. Although 14 values of $t_j^{Li,H}$, $0\leq j\leq 6$, are imposed as constraints in fitting experimental data, likely only eight of these have any impact on the fit, in the sense that parameters beyond those eight – t_j^{Li}, $0\leq j\leq 2$, and t_j^{H}, $0\leq j\leq 4$ – define the rotational g factor in ranges of R to which available spectral data are insensitive. Values of another 20 independently adjusted parameters – $U_{1,0}$, $U_{0,1}$, c_j with $1\leq j\leq 9$, $s_0^{Li,H}$, s_1^{H}, $u_1^{Li,H}$, $u_2^{Li,H}$, u_3^{H} and u_4^{H} – obtained from fitting wave numbers of 1000 data selected from various sources [117–121] are presented in table 3; as before, values of c_0, R_e and k_e are derived from values of $U_{1,0}$ and $U_{0,1}$, but values of $u_0^{Li,H}$ are evaluated from published data for adiabatic corrections [122].

According to application of Dunham's formalism to analysis of molecular spectra, as for GaH and H_2, these radial coefficients of seven types represent many Dunham coefficients Y_{kl} and their auxiliary coefficients Z_{kl} of various types that collectively allow wave numbers of observed transitions to be reproduced almost within their uncertainty of measurement through formula 54. Mostly because of inconsistency between reported values of frequencies of pure rotational transitions [118,119], the reduced standard deviation of the fit reported in table 3 is 1.25, slightly greater than unity that would be applicable with consistent data for which uncertainty of each measurement were carefully assigned.

In the present context of generation of consistent term coefficients Y_{kl} and Z_{kl} through coefficients in selected radial functions, the major points of interest in

Table 3. Coefficients of radial functions and other molecular parameters of LiH X $^1\Sigma^+$

c_0/m^{-1}	6572379.3 ± 5.6	s_0^{Li}	0.9126 ± 0.0181
c_1	-0.8970678 ± 0.0000057		
c_2	0.348233 ± 0.000040	s_0^{H}	-0.2612 ± 0.0029
c_3	-0.093085 ± 0.000196	s_1^{H}	-0.3733 ± 0.0195
c_4	-0.044426 ± 0.00087		
c_5	0.0765 ± 0.0027	$u_0^{\mathrm{Li}}/10^6\ \mathrm{m}^{-1}$	$[168.411 \pm 0.002]$
c_6	-0.1143 ± 0.0078	$u_1^{\mathrm{Li}}/10^6\ \mathrm{m}^{-1}$	-5.53900 ± 0.0082
c_7	-0.2078 ± 0.024	$u_2^{\mathrm{Li}}/10^6\ \mathrm{m}^{-1}$	6.357 ± 0.134
c_8	0.6024 ± 0.049	$u_0^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	$[12.829 \pm 0.002]$
c_9	-0.7538 ± 0.115	$u_1^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	-5.15624 ± 0.00096
$U_{0,1}/\mathrm{m}^{-1}\ \mathrm{u}$	662.708918 ± 0.000082	$u_2^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	4.923 ± 0.021
$U_{1,0}/\mathrm{m}^{-1}\ \mathrm{u}^{1/2}$	131993.551 ± 0.064	$u_3^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	-3.340 ± 0.051
$R_e/10^{-10}\ \mathrm{m}$	$1.59491242 \pm 0.00000020$	$u_4^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$	4.828 ± 0.158
$k_e/\mathrm{N\ m}^{-1}$	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}	$[1.28086 \pm 0.00047]$
t_2^{Li}	$[-1.2181 \pm 0.0022]$	t_2^{H}	$[-1.7927 \pm 0.00191]$
t_3^{Li}	$[1.077 \pm 0.022]$	t_3^{H}	$[2.0040 \pm 0.0088]$
t_4^{Li}	$[-1.710 \pm 0.106]$	t_4^{H}	$[-1.6797 \pm 0.0198]$
t_5^{Li}	$[3.546 \pm 0.160]$	t_5^{H}	$[2.375 \pm 0.033]$
t_6^{Li}	$[-2.586 \pm 0.34]$	t_6^{H}	$[-0.5685 \pm 0.079]$
t_7^{Li}	$[-6.825 \pm 0.65]$	t_7^{H}	$[-0.8264 \pm 0.042]$
$t_8^{\mathrm{Li}}\mathrm{t}_8^{\mathrm{Li}}$	$[6.37 \pm 0.31]$		

these results are comparisons of experimental and calculated values of extra-mechanical effects within the same context; alternative theoretical and computational approaches to evaluation of molecular energies and properties of ^{7}Li^{1}H impose no such radial functions in that generation [123,124]. From values of coefficients $s_{\mathrm{j}}^{\mathrm{Li,H}}$ we derive this formula for the vibrational g factor,

$$g_v = (-0.1291 \pm 0.0039) + (-0.3733 \pm 0.0195)z \tag{72}$$

valid within a range $R/10^{-10}\ \mathrm{m} = [1.17, 2.25]$ for comparison with a formula from fitted data from computations,

$$\begin{aligned} g_v = {} & (-0.136553 \pm 0.000056) + (-0.69064 \pm 0.00073)z \\ & + (0.6381 \pm 0.0038)z^2 + (0.0435 \pm 0.027)z^3 - (0.388 \pm 0.056)z^4 \\ & - (0.155 \pm 0.29)z^5 + (1.402 \pm 0.35)z^6 - (6.285 \pm 0.93)z^7 \\ & - (17.96 \pm 1.14)z^8 \end{aligned} \tag{73}$$

valid in a much larger range, $R/10^{-10}\ \mathrm{m} = [1.05, 3.0]$. Agreement of the constant terms is satisfactory, but the single further coefficient from experiment implies a slope only half that calculated theoretically, doubtless reflecting the truncation at a linear term. For adiabatic corrections we can compare not only the total function but also contributions of individual atomic centres. From fitted values of u_1^{Li} and u_2^{Li} in table 2 plus u_0^{Li} derived from published calculations [122], we produce the following formula to represent a radial function for adiabatic corrections associated with the lithium atomic centre independent of atomic mass,

$$\mathrm{V'Li(z)}/(hc)/\mathrm{u\ m^{-1}} = [92385.19] + (-3086.8 \pm 8.2)z + (3597 \pm 73)z^2 \tag{74}$$

compared with an exact polynomial representation of calculated points [122] that yields this formula:

$$\begin{aligned} & \mathrm{V'Li(z)}/(hc)/\mathrm{u\ m^{-1}} \\ & = 92385.19 - 3169.90z + 4896.87z^2 + 1987.27z^3 - 11905.13z^4 \\ & \quad - 37933.27z^5 + 71718.27z^6 + 74959.08z^7 \end{aligned} \tag{75}$$

Coefficients of z to various powers in these formulae differ from values of u_{j} in table 3 because the latter reflect a presence of a factor m_{e} in formula 47; all values of constant terms are derived from calculation [122], not from fits to frequency data. Coefficients of corresponding linear and quadratic terms in formulae 74 and 75 have comparable signs and magnitudes. From fitted values of u_j^{H}, $1 \le j \le 4$, in table 3 we derive analogously a corresponding formula to represent a radial function for adiabatic corrections associated with the hydrogen atomic centre,

$$\begin{aligned} \mathrm{V}'^{\mathrm{H}}(\mathrm{z})/(hc)/\mathrm{u\ m}^{-1} \\ &= [7035.2] + (-2828.48 \pm 0.52)z + (2688.2 \pm 11.5)z^2 \\ &\quad + (-1405 \pm 59)z^3 + (1331 \pm 187)z^4 \end{aligned} \tag{76}$$

The corresponding exact fit to calculated points [122] is

$$\begin{aligned} \mathrm{V}'^{\mathrm{H}}(\mathrm{z})/(hc)/\mathrm{u\ m}^{-1} \\ &= 7035.2 - 3160.75z + 5584.07z^2 + 13854.46z^3 - 100067.32z^4 \\ &\quad + 13622.76z^5 + 502328.20z^6 - 523003.44z^7 \end{aligned} \tag{77}$$

The sign and magnitude of the linear term in formula 76 concur moderately satisfactorily with those properties of a corresponding term in formula 77, but agreement between other corresponding terms is lacking. We compare the total adiabatic corrections for ^{6}Li^{1}H from a sum of corrections of separate atomic centres in formulae 74 and 76 divided by their masses,

$$\mathrm{V}'(z) = \mathrm{V}'^{\mathrm{Li}}(\mathrm{z})/M_{\mathrm{Li}} + \mathrm{V}'^{\mathrm{H}}(\mathrm{z})/M_{\mathrm{H}} \tag{78}$$

which yields this formula,

$$\begin{aligned} \mathrm{V}'(\mathrm{z})/(hc)/\mathrm{u\ m}^{-1} &= [22342.6] - 3311.8z + 3259.4z^2 - 1818.0z^3 \\ &\quad + 2628.0z^4 \end{aligned} \tag{79}$$

with a formula interpolated from points for the corresponding total calculated adiabatic corrections [122] for ^{6}Li^{1}H,

$$\begin{aligned} \mathrm{V}'(\mathrm{z})/(hc)/\mathrm{u\ m}^{-1} &= 22342.6 - 3722.1z + 6709.4z^2 + 16517z^3 - 115968z^4 \\ &\quad + 7699.5z^5 + 585535z^6 - 587860z^7 \end{aligned} \tag{80}$$

Like formulae for contributions to total adiabatic corrections from individual atomic centres above, the corresponding coefficients for the linear term have the same sign and comparable magnitude, but for subsequent coefficients agreement is lacking. The maximum region of validity of the experimental functions is the same as for the vibrational g factor, specified above, whereas the region for which the calculated points define the contributions and total adiabatic correction [122] is $R/10^{-10}\,\mathrm{m} = [1,3]$.

For comparison with our results in table 3, which presents values of 20 adjusted parameters with 15 parameters constrained to define the rotational g factor, Dulick et alii [115] required also 20 adjusted parameters, with a constrained parameter $\mathcal{D}_{\mathrm{e}}$ for the equilibrium binding energy for a function of potential energy having a modified Morse form. The latter parameter is specified as

$\mathcal{D}_e = 2028600\ \mathrm{m}^{-1}$ but this value varies $\sim 300\ \mathrm{m}^{-1}$ among various isotopic molecular species composed of ^{6}Li, ^{7}Li, ^{1}H and ^{2}H because each has a distinct value of $\mathcal{D}_e$ within that range. Although in this case the experimental curve of potential energy [115] conforms superficially to points from computations of molecular electronic structure [125] on the scale of that plot, with no discernible maximum or other anomaly, extrapolation to predict vibration-rotational transitions much beyond the range of $v = 6$ for ^{7}Li^{1}H, or $\sim 8.2 \times 10^5\ \mathrm{m}^{-1}$, must be subject to progressive propagation of error from measured transitions, apart from the variability of $\mathcal{D}_e$ that affects such a prediction increasingly on approach to the dissociation limit. The measured transitions define the lower two fifths of the range of energy to the dissociation limit. As for GaH [93], representations of empirical functions for LiH [115] to take into account extra-mechanical effects have the form of truncated polynomials in displacement, $R - R_e$; their claimed maximum range of validity is $R/10^{-10}\ \mathrm{m} = [1.16, 2.48]$. Beyond that range such polynomials, of degree sixth and cubic, tend to diverge rapidly, much more rapidly than a polynomial in z, as published plots clearly demonstrate [115]. This behaviour confirms the superiority of properties of variable z; for instance an increment from $R/10^{-10}$ m from 3 to 4 is four times as large as the corresponding increment in z for LiH from 0.61 to 0.86. The accuracy of prediction of wave numbers of transitions involving states with terms greater than $\sim 8.5 \times 10^5\ \mathrm{m}^{-1}$ becomes thereby progressively and severely diminished. A ratio of error due to uncertainty in $\mathcal{D}_e$ to the best claimed accuracy of actual measurements for LiH, $0.05\ \mathrm{m}^{-1}$ [115], is ~ 6000, but the absolute and relative accuracy of predictions for even moderate v due to invalidity of radial functions for extra-mechanical effects expressed as polynomials in displacement is much worse. Despite the apparent quality of the function for potential energy of modified Morse type [115], which still possesses an incorrect limiting dependence on R toward the dissociation limit, the quality of predictions beyond the range of measured transitions is hence highly doubtful. Apparent agreement between this modified Morse curve and computationally derived points [125], themselves subject to error, must be regarded as fortuitous: over much of the illustrated range before an avoided crossing at $R_x = 3.857 \times 10^{-10}$ m with a curve for potential energy of state A $^1\Sigma^+$ [126], there is a strong contribution to molecular binding from coulombic attraction between essentially atomic ions, for which the potential energy varies according to R^{-1} and for which an exponential representation is consequently poor. For $R_e < R < R_x$, the curve for potential energy thus has such an inverse dependence on internuclear distance heading toward an asymptote corresponding to a limit of dissociation into ions Li$^+$ and H$^-$, whereas after that point the adiabatic curve of potential energy for the electronic ground state proceeds toward an asymptotic limit of dissociation at smaller energy into neutral atoms Li and H [127]. A postulated advantage of accurate prediction of wave numbers of transitions far above the measured range through representing potential energy in a modified Morse form is plainly illusory.

For vibration-rotational data of LiH in a smaller set, an approach of optimal fitting parameters for extra-mechanical effects has also been applied [85]; as for other fits described above, 20 selected parameters were adjusted to reproduce satisfactorily the data, numbering 583 rather than 1000 for which results appear in table 3. As these data sets differ markedly, comparison of parameters is impracticable.

9. CARBON OXIDE, CO

Here we consider mainly intensities of vibration-rotational spectra in absorption; as a function for potential energy is a prerequisite for calculations involving intensities, we necessarily include this aspect. In contrast with measurements of wave numbers of reasonably spectral lines in an infrared spectrum of a diatomic molecule, for which relative precision $\sim 10^{-6}$ is routinely achievable, for measurement of a strength of a particular spectral line to attain a relative precision superior to one per cent is exceptional; through the smoothing effect of multiple data contributing to this quantity, the corresponding strength of a band might thus attain a relative precision 0.1 per cent at best. The relative precision of a strength of a line in a Raman spectrum is generally worse. Expectation values of quantities from Stark and Zeeman effects might be measured with precision of order 0.1 per cent at best; in such cases few measurements are practicable, hence precluding significant improvement in derived quantities through a smoothing effect. There thus exists almost no need of refined treatment of intensities in the manner of van Vleck's extension of Dunham's theory for data of frequency type. Dunham's approach in his first two publications indeed survives in an almost similar form for analysis of intensities of infrared spectral lines of the best contemporary quality.

Dunham's consideration of available spectra of HCl in 1930 [1,2] resulted in production of a radial function for electric dipolar moment that we express in a contemporary form, similar to that in formula 56 but in terms of variable x, defined in formula 15, instead of z, defined in formula 21:

$$\mathrm{p}(x)/10^{-30}\ \mathrm{C\ m} = p_0 + 3.54x + \{0.177 \text{ or } 7.61\}x^2 \tag{81}$$

At that time the permanent electric dipolar moment p_0 of HCl had already been estimated to be $\sim 3.59 \times 10^{-30}$ C m [128], but Dunham made no use of this value; hence we leave p_0 in symbolic form. One or other value of coefficient p_2 depends on a ratio $\langle 1/\mathrm{p}(x)|0\rangle/\langle 2|\mathrm{p}(x)|0\rangle$ of pure vibrational matrix elements of electric dipolar moment between the vibrational ground state and vibrationally excited state $v=1$ or 2. We compare these data with an extended radial function derived from 33 expectation values and matrix elements in a comprehensive statistical treatment [129],

$$\begin{aligned}\mathrm{p}(x)/10^{-30}\ \mathrm{C\ m} = {} & (3.64587 \pm 0.00025) + (4.12334 \pm 0.00147)x \\ & + (0.00688 \pm 0.0177)x^2 + (-5.110 \pm 0.044)x^3 \\ & + (-3.065 \pm 0.088)x^4 + (-1.174 \pm 0.142)x^5 \\ & + (-1.46 \pm 0.24)x^6 + (1.17 \pm 0.69)x^7\end{aligned} \tag{82}$$

Apart from the greatly increased precision of coefficients reflecting improved spectral resolution over 70 years between generation of these functions, one discerns that early values of p_0 and p_1 are roughly correct and that one possible value that Dunham [2] proposed for p_2 has a magnitude comparable with the current value.

The quandary that Dunham confronted in proposing an alternative value of p_2 was solved through the work of Herman and Wallis [130] in the spirit of Dunham's symbolic approach. A major problem affecting the derivation of radial functions from data of intensity type is that the strength of a spectral line or band is proportional to a square of a matrix element, making its sign directly indeterminate. Explicitly, for a gaseous sample of a diatomic molecular species in electronic state $X\,^1\Sigma^+$ in absorption at temperature T, the strength S_l of a line due to a spectral transition from a state $|0, J''\rangle$ to another state $|v', J'\rangle$ in a vibration-rotational spectrum is expressed according to this formula [13],

$$S_l = (8\pi^3/3hc)[\exp(-hcE_{0\mathrm{J}}/k_BT)/4\pi\varepsilon_0 Q]\tilde{\nu}_l[1-\exp(-hc\tilde{\nu}_1/k_BT)] \\ \times |\iota|\langle v'J'|\mathrm{p}(x)|0, J''\rangle|^2 \tag{83}$$

in which appear fundamental physical constants h, c, k_B and ε_0, total partition function Q, value of spectral term $E_{0,\mathrm{J}}$ of an initial state $|0, J'\rangle$ of a transition relative to the minimum term $E_{0,0}$, and wave number $\tilde{\nu}_l$ of a spectral line representing that transition; $\iota \equiv \frac{1}{2}[J'(J'+1)-J''(J''+1)]$ is a running number of value $J''+1$ for a line in branch R or $-J''$ for a line in branch P. In $|\langle v'J'|\mathrm{p}(x)|0, J''\rangle|^2$ that is the square of an experimental matrix element for a transition between specified vibration-rotational states, $\mathrm{p}(x)$ is a radial function for electric dipolar moment of an absorbing molecular species in terms of reduced displacement x, as in formula 82 and equivalent to formula 56 for $\mathrm{p}(z)$. The rotational dependence is supposed factorable according to a formula [130,13]

$$|\langle v'J'|\mathrm{p}(x)|0, J''\rangle|^2 = |\langle v'|\mathrm{p}(x)|0\rangle|^2(1 + C_0^{v'}\iota + D_0^{v'}\iota^2 + \ldots) \tag{84}$$

in which $|\langle v'|\mathrm{p}(x)|0\rangle|^2$ is the square of the pure vibrational matrix element of electric dipolar moment; the latter quantity is coefficient to a Herman-Wallis factor containing, in a representation as a truncated polynomial up to a quadratic term, Herman-Wallis coefficients $C_0^{v'}$ and $D_0^{v'}$. In the latter quantities that are composite functions [13] containing parameters for potential energy in $\mathrm{V}(x)$ or $\mathrm{V}(z)$ and for dipolar moment $\mathrm{p}(x)$ or $\mathrm{p}(z)$ in the numerator and with matrix element $\langle v'|\mathrm{p}(x)|0\rangle$ in the denominator, Herman and Wallis demonstrated that vibration-rotational interaction causes strengths of lines to vary linearly with coefficients p_j. Fitting squared vibration-rotational matrix elements $|\langle v'J'|\mathrm{p}(x)|0, J''\rangle|^2$ as a function of ι, according to formula 84, hence yields essentially the squared vibrational matrix element $|\langle v'|\mathrm{p}(x)|0\rangle|^2$ as a constant term and parameters $C_0^{v'}$ and $D_0^{v'}$ as coefficients of ι and ι^2; comparison of calculated values of the latter quantities as functions of coefficients p_j and $\langle v'|\mathrm{p}(x)|0\rangle$ – a signed quantity – with the corresponding experimental values then yields the latter quantities according to the best match [13], as we illustrate below.

To complete the set of formulae required in analysis of intensities of spectral lines in absorption, an experimental measure of a band strength S_b is a sum of measured strengths S_l of all lines in that band,

$$S_b = \sum S_l \tag{85}$$

whereas a theoretical measure relates to the pure vibrational matrix element of electric dipolar moment,

$$S_b = 8\pi^3 \tilde{\nu}_o |\langle v'|\mathrm{p}(x)|0\rangle|^2/(3hc4\pi\varepsilon_0) \tag{86}$$

in which $\tilde{\nu}_o$ is the wave number characterising the origin of the band. A line strength is derived from integrated absorbance of a particular spectral line, a known number density N of molecules per unit volume in a gaseous sample at temperature T and the effective length ℓ of optical path:

$$S_l = (1/N\ell)\int \ln[\mathrm{I}_0(\tilde{\nu})/\mathrm{I}(\tilde{\nu})]d\tilde{\nu} \tag{87}$$

On the basis of these formulae one can convert measurements of area, which equals the integral in the latter formula, under spectral lines into values of coefficients in a selected radial function for electric dipolar moment for a polar diatomic molecular species. Just such an exercise resulted in the formula for that radial function [129] of HCl in formula 82, combining in this case other data for expectation values $\langle 0, J|\mathrm{p}(x)|0, J\rangle$ from measurements of the Stark effect as mentioned above. For applications involving these vibration-rotational matrix elements in emission spectra, the Einstein coefficients for spontaneous emission conform to this relation,

$$A_{\mathrm{nm}} = 16\pi^3 \tilde{\nu}^3 |\langle n|\mathrm{p}(x)|m\rangle|^2 |\iota|/[3h\varepsilon_0(2J' + 1)] \tag{88}$$

in which n and m denote collectively the vibrational and rotational quantum numbers in sets specifying states combining in a transition from n to m.

A radial function for electric dipolar moment for a hydrogen halide appears to have a single extremum, near the equilibrium internuclear distance R_e, such that, for $^1H^{35}Cl$ for instance in formula 82, $\mathrm{p}(x) = 0$ for both the united atom ^{36}Ar at $R = 0$ or $x = -1$ and the separate atoms ^1H and ^{35}Cl as R or $x \to \infty$, but not elsewhere. The behaviour of this function on approaching these limits is known [13]: as $R \to 0$ for all neutral diatomic molecules, $\mathrm{p}(R) \propto R^3$, whereas as $R \to \infty$, $\mathrm{p}(R) \propto R^{-7}$ if states of both separate atoms have total electronic angular momentum $< \hbar$ or $\mathrm{p}(R) \propto R^{-4}$ otherwise; for instance the former condition is applicable to LiH, whereas the latter condition is applicable to hydrogen halides, CO, NO and many other species. For HF, HCl and HBr, the extremum in $\mathrm{p}(x)$ occurs at $R > R_e$ [13]; accordingly p_1 or the slope of $\mathrm{p}(x)$ at R_e is positive. In contrast, for HI the extremum in $\mathrm{p}(x)$ occurs at $R < R_e$, with a small negative slope near R_e, confirmed by both precise calculations of molecular electronic structure and experimental data [131]; as in the calculations relativistic effects were included to obtain that result, one might consider the qualitatively different slope to be a relativistic effect.

Some data for spectral intensities of HCl for $v > 3$ have questionable quality, whereas recent measurements of intensities of CO are generally superior; for this reason we consider the latter molecule in some detail. Carbon oxide CO plays an important role in combustion of carbonaceous fuels and terrestrial processes in the atmosphere, and has been detected through its spectral lines for pure rotational transitions in many extra-terrestrial environments. Accordingly, a knowledge of radiative properties of CO is extremely important in relation to both investigation of dynamics of combustion processes and modeling of radiative properties of the terrestrial atmosphere. Like a commercially and technologically important laser based on carbon dioxide CO_2, a laser with working substance CO oscillates on vibration-rotational transitions. Most known vibration-rotational transitions [132] of diatomic molecules that exhibit stimulated emission occur in the fundamental band, $v' = 1 \rightarrow v'' = 0$, or in sequences with $\Delta v = 1$. Most transitions for which laser action is reported involve lines in P branches because these lines are favoured both by non-equilibrium conditions of extensive vibrational excitation but by small rotational excitation and a less stringent condition on rotational degeneracies: g_n as $2J' + 1$ can be $2J - 1$ for a P branch rather than $2\,J + 3$ for an R branch; laser emission in a P branch serves simultaneously to decrease vibrational excitation and to increase rotational energy, facilitating an approach to thermal equilibrium [13]. For $^{12}C^{16}O$ about 700 transitions have been measured in bands $1 \rightarrow 0$ up to $37 \rightarrow 36$, covering discontinuously a range $1.2 \leq \tilde{\nu}/10^5\ m^{-1} \leq 2.0$, and even some laser lines with $\Delta v = 2$ have been observed [133]; more than 100 laser transitions of CO in other isotopic species are also reported [132]. A device that provided those sequences with $\Delta v = 1$ in laser action also produced emission of CO in seven isotopic variants with sequences $\Delta v = 1$, $\Delta v = 2$ and $\Delta v = 3$ up to $v' = 41$ [134]; although parameters calculated from several thousand transitions were described [134] as Dunham coefficients, implying Y_{kl} according to formula 8, because constraints between these parameters were not applied, they actually correspond to coefficients A_{kl} in formula 2.

The fundamental vibration-rotational band of CO in the mid infrared region was the first spectral feature of a gaseous sample of a diatomic molecular substance to be measured in this region [135]; subsequent measurements exploited progressively increasing spectral resolution and accuracy of the wave number scale. Overtone spectra of CO exhibit progressively decreasing strengths of bands [99], such that, whereas the first overtone at a conventional boundary of the mid infrared region is readily measurable, the second overtone in the near infrared requires an extended optical path; the third overtone approaches the limits of detectability with an optical path 100 m and a gaseous sample at approximately atmospheric pressure, and with conventional methods for absorption spectra. Attempting to detect the fourth overtone with product of length of absorbing path and pressure equal to 3000 m bar, Herzberg and Rao [136] searched unsuccessfully, like our subsequent attempt [99]: $1\ \text{bar} = 10^5\ N\ m^{-2}$. Eventual success [137] in detecting band $v' = 5 - v'' = 0$ was attained through adapting a *cavity-ringdown* spectral technique [138] to the near infrared region; intensities of only lines in branch P of this band were measurable, but estimates of the strength of each line in a series P_3–P_{18} from fitting its profile to a lorentzian shape enabled deduction of a pure vibrational matrix element $\langle 5|p(x)|0\rangle$ consistent with Herman-Wallis coefficient C_0^5 and a strength of the entire

Table 4. Band origin, pure vibrational matrix element and strength of vibration-rotational bands of $^{12}C^{16}O$

Band	$\tilde{\nu}_0/m^{-1}$	$\langle v'\|p(x)\|0\rangle$/C m	S_b/m
0 – 0		3.6632×10^{-31}	
1 – 0	214327.11	-3.53×10^{-31}	1.00×10^{-19}
2 – 0	426006.22	2.22×10^{-32}	7.83×10^{-22}
3 – 0	635043.91	-1.36×10^{-33}	4.42×10^{-24}
4 – 0	841446.93	6.95×10^{-35}	1.53×10^{-26}
5 – 0	1045222.22	3.62×10^{-36}	6.13×10^{-29}

vibration-rotational band. Results of such measurements for all vibration-rotational bands originating in the vibrational ground state [99,137], with a further expectation value for that ground state from experiments on a molecular beam [139], are collected in table 4.

To convert these data into radial functions, one might apply algebraic expressions for vibrational matrix elements of x to various powers, of form such as

$$\langle 1|x|0\rangle = \gamma/\sqrt{2} + \sqrt{2}\gamma^{3/2}(11a_1^2/32 - 3a_2/8) + \ldots \tag{89}$$

in which appear coefficients a_j for potential energy according to Dunham's function in formula 16 and γ as defined in relation to formula 61. We evaluated values of corresponding coefficients c_j up to c_{12} from a fit of 16947 data up to $v=41$ and $J\sim115$, including some duplication of vibration-rotational and pure rotational transitions, for CO in isotopic variants with $^{12,13,14}C$ and $^{16,17,18}O$ in various combinations to parameters in radial functions for potential energy, adiabatic corrections and vibrational g factors, constraining parameters $t_j^{C,O}$ related to the rotational g factor to values consistent with computations of molecular electronic structure [99]. Likely because procedure Radiatom lacks full contributions to some Dunham coefficients Y_{kl} that require calculation according to hypervirial perturbation theory up to order 26 (and consequently that severely tax available computational resources), slight systematic discrepancies [99] exist between calculated and measured wave numbers of transitions involving $v>39$, but remain within 3.5 times their nominal uncertainties σ; the overall reduced standard deviation of the fit to 20 adjustable and 10 constrained parameters was still acceptable. This data set would benefit from thorough reappraisal, but original data for many vibration-rotational transitions are unavailable and secondary sources contain slightly disparate values of both wave numbers and their uncertainties – hence the duplication. Nevertheless for calculations involving vibrational states up to $v=5$, the derived values of parameters c_j up to $j=8$ are sufficient and reliable, and thus serve for calculations involving matrix elements of electric dipolar moment with expressions of the type in formula 89. These expressions are readily generated to any desired extent of v or x^l [44] to sufficient precision involving terms with γ to increasing exponents; as for all known stable neutral diatomic molecular species γ has values less than 0.026 – for instance, $\gamma = 0.0070838$ for $^{12}C^{16}O$ – convergence within a desired precision is generally rapid. A theoretical expression for a pure vibrational matrix element of electric dipolar moment $p(x)$ expressed as a polynomial in terms of these matrix elements of x^l is simply

$$\langle v'|p(x)|0\rangle = \sum_{j=0} p_j \langle v'|x^l|0\rangle \tag{90}$$

including as many terms in the sum as necessary, generally $v'+1$ in total. On the basis of these experimental numerical values of vibrational matrix elements and algebraic expressions for $\langle v'|x^l|0\rangle$ into which numerical values of coefficients a_j and γ are inserted, one solves a system of simultaneous linear equations to evaluate coefficients p_j. As these parameters are not overdetermined, direct statistical methods are inapplicable to yield required uncertainties of evaluated parameters; in such a case a Monte-Carlo method [140] of analysis of error propagated from values of pure vibrational matrix elements to coefficients p_j is suitable. In general, signs of $\langle v'|p(x)|0\rangle$ are unknown because experiments yield their magnitudes or squares, according to formula 84 for instance. One then applies these derived values of coefficients p_j in sets depending on a chosen sign of each value of $\langle v'|p(x)|0\rangle$, relative to a particular sign chosen typically for p_0 or $\langle 0|p(x)|0\rangle$, to calculate coefficients $C_0^{v'}$ and $D_0^{v'}$ according to algebraic expressions [13,44] in terms of coefficients a_j pertaining to potential energy and γ, coefficients p_j for electric dipolar moment and values of $\langle v'|p(x)|0\rangle$ with one or other sign. Signs of $\langle v'|p(x)|0\rangle$ in a particular set that yield best agreement between thus calculated values of $C_0^{v'}$ and $D_0^{v'}$ and their experimental counterparts from formula 84 are hence preferable, thereby evaluating elegantly the radial function $p(x)$ for electric dipolar moment. Instead of coefficients a_j and p_j of x to various powers, one can naturally work with coefficients c_j and p_j (according to formula 56) of z to various powers, as the corresponding algebraic expressions for vibrational matrix elements and Herman-Wallis coefficients are just as readily generated [44] in terms of these quantities.

As an illustration of this approach to solution of a radial function $p(x)$ for $^{12}C^{16}O$, we present in table 5 experimental [99] and calculated values of Herman-Wallis coefficients $C_0^{v'}$ and $D_0^{v'}$, calculated on the basis of this radial

Table 5. Experimental and calculated values of Herman-Wallis coefficients $C_0^{v'}$ and $D_0^{v'}$ for $^{12}C^{16}O$

band $v'-0$	$C_0^{v'}/10^{-2}$		$D_0^{v'}/10^{-4}$	
	exp'l	calc'd	exp'l	calc'd
0 – 0		—		−2.05
1 – 0	0.024 ± 0.021	0.0196	—	0.067
2 – 0	0.533 ± 0.014	0.496	0.44 ± 0.10	0.35
3 – 0	1.153 ± 0.025	1.210	1.03 ± 0.18	0.99
4 – 0	3.370 ± 0.033	3.284	4.27 ± 0.34	4.3
5 – 0	∼ −10	−9.33	—	17.6

function p(x) derived from experiment [135];

$$\mathrm{p}(x)/10^{-30}\ \mathrm{C\ m} = 0.407871 - 11.8634x + 1.3060x^2 + 13.378x^3 - 2.740x^4 - 0.17x^5 \tag{91}$$

this function has a range $R/10^{-10}$ m of validity [0.99, 1.33]. A value of C_0^5 was indicated only roughly from preliminary experiment [137]; experimental values of D_0^0, D_0^1 and D_0^5 are unavailable.

Changing the sign of $\langle 5|\mathrm{p}(x)|0\rangle$ from positive to negative correspondingly alters the sign of p_5, the value calculated for C_0^5 from -0.093 to $+0.093$ and the value calculated for D_0^4 from 0.00043 to 0.00037, but affects other calculated values negligibly. As the latter calculated value is almost inconsistent with an experimental value of D_0^4 specified in table 5, the negative value of C_0^5 is clearly preferable, even though indicated only roughly in the reported experiment [137]. Chackerian and Tipping [141] predicted $\langle 5|\mathrm{p}(x)|0\rangle = 6.588\times10^{-36}$ C m, $C_0^5 = -0.0529$ and $D_0^5 = 0.00040$; because the former value is only about twice the experimental value $(3.62\pm0.3)\times10^{-36}$ C m, we might expect their predictions $\langle 6|\mathrm{p}(x)|0\rangle = -3.66\times10^{-36}$ C m, $C_0^6 = -0.014$ and $D_0^5 = -0.00014$ for band 6 – 0 to have comparable reliability. The ratios of strengths between successive vibration-rotational bands from experiment are thus 128, 177, 289, 250. On a basis of a predicted strength 6.25×10^{-29} m for band 6 – 0 [141], the fifth overtone is remarkably predicted to have almost the same intensity as the fourth overtone. We contrast these ratios of strengths of vibration-rotational bands of $^{12}\mathrm{C}^{16}\mathrm{O}$ with those of $^{14}\mathrm{N}^{16}\mathrm{O}$ – 61.2, 48.5, 23.3, 13.4, 8.6 [142] – which thus decrease regularly in the same order of increasing vibrational quantum number v. The radial functions for electric dipolar moment of NO and CO share common features of two extrema, with a reversal of polarity between these two extrema and small magnitudes of permanent electric moment p(R_e). In each case the polarities, $^-\mathrm{NO}^+$ and $^-\mathrm{CO}^+$, at that condition contradict expectations from crude consideration of conventional electronegativities.

As an alternative procedure to predict coefficients of a radial function p(x) for electric dipolar moment, one might attempt to convert the latter function from polynomial form, as in formula 91, which has unreliable properties beyond its range of validity from experimental data, into a rational function [13] that conforms to properties of electric dipolar moment as a function of internuclear distance R towards limits of united and separate atoms. When such a rational function is constrained to yield the values of its derivatives the same as coefficients p_j in a polynomial representation, that rational function becomes a Padé approximant. For CO an appropriate formula that conforms to properties described above would be

$$\mathrm{p}(x) = p_0(1+x)^3 \Big/ \left(1 + \sum_{j=1} q_j x^j + C_\infty x^7\right) \tag{92}$$

in which in the sum in the denominator as many terms are taken as necessary; the numerator bestows a property p(x)→0 proportional to R^3 as R→0, whereas the last term in the denominator ensures that $\mathrm{p}(x) \rightarrow 0$ as R becomes large, in practice greater than $\sim 10R_e$. Coefficient C_∞ might be accorded a value based on some knowledge of the behaviour of this radial function at large R, such as a value of p from calculations of molecular electronic structure; such a value has no effect on recalculated values of p_j or $\langle j|\mathrm{p}(x)|0\rangle$ for $j<7$. Application of this formula for CO yields a function that suffers severely from a pole within a region of interest, which makes it unusable. An alternative form that might be applicable to a radial function for electric dipolar moment that possesses two extrema in a region defined by experiment, with a reversal of polarity between distances of these extrema at x_0, is

$$\mathrm{p}(x) = p_0(1+x)^3(x-x_0)/\left(-x_0 + \sum_{j=1} q_j x^j + C_\infty x^8\right) \tag{93}$$

but this formula applied to CO also suffers from poles dictated by roots in the denominator within the region of interest. Under these conditions one might be forgiven for neglecting the behaviour of $\mathrm{p}(x)$ as $x \rightarrow -1$ or $R \rightarrow 0$ because this region lacks chemical interest; a rational function that still qualifies as a Padé approximant and retains the correct limiting behaviour as x or $R \rightarrow \infty$, which is of chemical interest, has this form for CO that has a reversal of polarity at $x = x_0$:

$$\mathrm{p}(x) = p_0(x+1)(x/x_0 - 1)/\left(1 + \sum_{j=1} q_j x^j + C_\infty x^6\right) \tag{94}$$

Although transformation of coefficients p_j into coefficients q_j is readily practicable, the resulting values for CO adopt unwieldy magnitudes. Chackerian and Tipping [141] fitted a function of the latter form from experimental and theoretical (computations of molecular electronic structure) information in judicious combination, according to which they calculated vibration-rotational matrix elements for transitions in bands 5 – 0 and 6 – 0; fitting the latter values with formula 84 yielded the values of quantities presented above. Rational functions, such as those in formulae 92 – 94 or others, transcend the spirit of Dunham's approach because their construction incorporates physical knowledge of a quantity that is superfluous for invocation of a mere truncated polynomial.

10. DISCUSSION

When Dunham [4,5] presented formula 8 for vibration-rotational terms, he derived a functional $v + ½$ explicitly because in his JBKW formulation the addend ½ results from exact solution of an integral. In contrast, Dunham assumed a functional $K(K+1)$, equivalent to $J(J+1)$ in contemporary notation, to contain a quantum number K, now J, for rotational angular momentum. To generate an effective potential energy comprising both internuclear potential energy V(R) and kinetic energy $\hbar^2 J(J+1)/2\mu R^2$), Dunham expressed R in the latter denominator as $R_e(1+x)$ and then expanded the resulting denominator about $x=0$ as follows:

$$R_e^{-2}/(1+x)^2 \approx R_e^{-2}(1-2x+3x^2-4x^3+\ldots) \tag{95}$$

Dunham then combined these terms with corresponding terms in V(x) through rotationally dependent coefficients $a_j(J)$ for potential energy to produce his general expressions for term coefficients Y_{kl}. Each expression for a further such coefficient Y_{kl} in a sequence $Y_{k,l}$, $Y_{k,l+1}$, $Y_{k,l+2}$… contains a factor γ^2 that, with $\gamma \ll 1$, ensures rapid convergence; under these conditions inclusion of a set of Y_{kl} down to $Y_{0,2k}$ assures that any error due to the approximation in formula 95 is negligible in comparison with experimental error due to measurement of frequency data; a particular test appears in discussion of spectral data of GaH above. In an alternative procedure for analysis of vibration-rotational spectral data called *deformationally self-consistent*, Molski employed algebraic expressions for term coefficients $Y_{k,0}$ but employed a numerical scheme to generate the rotational dependence of spectral terms [143] that essentially circumvents the approximation implied in an expansion in formula 95. Comparison of results for NaCl under controlled conditions [143] demonstrates no advantage for this approach; a slight disadvantage arises from an algorithm for estimation of non-linear parameters. Molski's approach has produced questionable results in several cases [144] and appears unreliable for its intended purpose.

Although authors [74,75] have claimed that a generator-coordinate theory yields an expression for spectral terms exactly of Dunham's form, as in formula 8, in which however term coefficients Y_{kl}^{GCA} encompass intrinsically effects of at least adiabatic corrections, it is unclear from those papers how the functionals of v and J in their expression for E_{vJ}^{i} arise. As mentioned above, Dunham [4,5] derived the addend ½ of v but assumed the form $K(K+1)$ instead of deriving it; authors of the generator-coordinate theory [74,75] appear to have assumed the forms of both functionals $(v+½)$ and $J(J+1)$. In lack of explicit expressions for any coefficient Y_{kl}^{GCA} that differs from results from application of classical mechanics one can not identify justification for these details.

The effective hamiltonian in formula 29 incorporates approximations that we here consider. Apart from a term $V''(R)$ that originates in nonadiabatic effects [67] beyond those taken into account through the rotational and vibrational g factors, other contributions arise that become amalgamated into that term. Replacement of nuclear masses by atomic masses within factors in terms for kinetic energy for motion both along and perpendicular to the internuclear axis yields a term of this form for the atomic reduced mass,

$$\mu^{-1} = [(m_a + Z_a m_e) + (m_b + Z_b m_e)]/[(m_a + Z_a m_e) + (m_b + Z_b m_e)] \tag{96}$$

in which m_a and m_b are nuclear masses of atomic centres A and B respectively. The relation of this term to the nuclear reduced mass μ_n is [66]

$$\mu^{-1} \cong [1 - m_e(Z_a m_b/m_a + Z_b m_a/m_b)/(m_a + m_b)]/\mu_n \tag{97}$$

As the subtrahend in this numerator has clearly the form of a ratio of electronic and nuclear masses, its effect can become absorbed within $V''(R)$ that contains contributions of like ratio of electronic and nuclear mass. Use of atomic rather than nuclear masses in the adiabatic correction $V'(R)$ in formula 31 yields an analogous correction that becomes likewise absorbed within $V''(R)$, and eventually neglected at present. Practical application of an effective hamiltonian for atoms with atomic number over a large range requires that one employ atomic rather than nuclear masses because atomic mass is accurately measured directly in experiment and because derivation of nuclear mass from such a quantity would involve not only subtracting electronic mass but also taking into account the binding energy of each electron. The latter quantity might have an associated error much larger than the imprecision of known atomic masses [145]; the relative precision of an atomic mass, 1.0×10^{-11}, is best for ^{16}O, and has typically a value $\sim 10^{-8}$ for other stable nuclides. For comparison the best measurements [146] of frequencies associated with vibration-rotational transitions have a relative precision $\sim 2 \times 10^{-10}$, although a relative precision for superior vibration-rotational transitions is typically $\sim 10^{-7}$, and approaches $\sim 10^{-8}$ for superior measurements of pure rotational [147] and vibration-rotational [148] transitions. As these relative precisions of measurements of mass and of frequency or wave number have clearly comparable ranges, the numerical significance of parameters independent of isotopic mass that are intended to reproduce accurate experimental measurements of wave number demonstrably depends critically on the values of atomic and electronic masses employed in deriving those parameters. Incorporation of precise further data into a set previously subjected to analysis typically requires for their reproduction parameters of increased number and of various types. For instance, for 17 pure rotational and 1223 vibration-rotational transitions of $^{23}Na^{35}Cl$ and $^{23}Na^{37}Cl$ within ranges $v \leq 8$ and $J \leq 120$, six independent fitted parameters, specifically R_e, k_e and $c_1 - c_4$, with two constrained parameters – $t_0^{Na,Cl}$ estimated from electric dipolar moment and a rotational g factor nearly zero, suffice to reproduce the wave numbers for which the best relative precision is 3×10^{-7} [81]. Addition of 189 pure rotational lines of these isotopic species [149], within ranges $v \leq 4$ and $J \leq 76$ but with relative precision up to 3×10^{-8}, requires further parameters; not only c_5 and c_6 for potential energy, reflecting enhanced sensitivity of the entire set of data to effects of centrifugal distortion, but also a parameter t_1^{Cl} related to the rotational g factor and a parameter u_1^{Cl} associated with adiabatic corrections, reflecting enhanced sensitivity of additional data to isotopic effects associated with Cl, become evaluated. These four additional parameters are essential even though all these further transitions involve vibrational and rotational states well within the previously existing range; there is no indication that further nonadiabatic effects, present in $V''(R)$, are required to be taken into account in this fit, consistent with $(m_e/\mu)^2 \sim 10^{-9}$ for NaCl being smaller than the best precision. Values of these parameters obtained from fits of data with Radiatom I, with the corresponding reduced standard deviations of the respective fits are presented in table 6; all parameters therein convey the same significance as in preceding tables 1 – 3. Comparison of values of the same parameters in the separate fits indicates that only small changes occur; hence for corresponding parameters these fits are reasonably stable. Because the

Table 6. Coefficients of radial functions and other molecular parameters of NaCl X $^1\Sigma^+$, depending on extent of data set and constrained parameters

Parameter	1223 data, $[t_0^{\mathrm{Na}}, t_0^{\mathrm{Cl}}]$	1412 data, $[t_0^{\mathrm{Na}}, t_0^{\mathrm{Cl}}]$	1412 data, $[t_0^{\mathrm{Na}}]$
c_0/m^{-1}	15247257 ± 18	15247401 ± 22	15247425 ± 24
c_1	−2.076785 ± 0.000037	−2.0768284 ± 0.0000095	−2.0768239 ± 0.0000095
c_2	2.54160 ± 0.00027	2.53836 ± 0.00048	2.53836 ± 0.00048
c_3	−1.8567 ± 0.0020	−1.84459 ± 0.00162	−1.84459 ± 0.00162
c_4	−0.2888 ± 0.0176	0.0198 ± 0.042	0.0195 ± 0.042
c_5	…	1.97 ± 0.29	1.975 ± 0.29
c_6	…	−2.21 ± 0.41	−2.22 ± 0.41
s_0^{Cl}	…	…	−0.238 ± 0.032
t_0^{Na}	[0.81]	[0.81]	[0.727]
t_0^{Cl}	[−0.77]	[−0.77]	−0.8527 ± 0.0082
t_1^{Cl}	…	−1.685 ± 0.067	…
$u_1^{\mathrm{Cl}}/10^6\mathrm{m}^{-1}$	…	−1.240 ± 0.126	…
$U_{0,1}/\mathrm{m}^{-1}\ \mathrm{u}$	302.465982 ± 0.000047	302.466455 ± 0.000039	302.467076 ± 0.000039
$U_{1,0}/\mathrm{m}^{-1}\ \mathrm{u}^{1/2}$	135820.124 ± 0.091	135820.873 ± 0.106	135821.120 ± 0.115
$R_e/10^{-10}\ \mathrm{m}$	2.36080425 ± 0.00000058	2.36080240 ± 0.00000057	2.36079998 ± 0.00000057
$k_e/\mathrm{N\ m}^{-1}$	108.687209 ± 0.000147	108.688406 ± 0.000171	108.688801 ± 0.000184
$\hat{\sigma}$	0.921	0.880	0.881

additional pure rotational data [149] are so precise, we avoided constraining a value of t_0^{Cl} in a further fit. With a known precise value of p_0 of ^{23}Na^{35}Cl [143] and fitted value of t_0^{Cl} in formulae 66 and 67, we calculate $g_r(R_e) = 0.00741 \pm 0.00060$ and t_0^{Na}; the latter value was included as a constraint in the fitting until convergence was attained. This value of g_r for ^{23}Na^{35}Cl is a genuine prediction as no value is known from other experiment or calculation, but its reliability rests on the assumption of negligible adiabatic corrections as explained above for GeS.

In contrast, the precision of measurement of intensity of spectral lines has increased little in the past half century; most of that minor increase reflects improved spectral resolution in the frequency domain, in many cases through either a Fourier transform of interferometric measurements in a distance domain with continuous sources of radiation or use of infrared lasers; in either case a spectral feature associated with a particular transition between discrete vibration-rotational states might be optimally isolated and well defined, with minimal distortion of shape and area due to a measuring device. Even the best strengths of individual isolated lines, measured essentially as an area under a spectral curve, are likely to have a relative precision worse than 10^{-3}; in cases of weak lines for which merely increasing the concentration or length of absorbing path is impracticable, or of difficult samples such as transient species, one might have reluctantly to accept a relative precision even $\sim 10^{-1}$. Under these conditions one has clearly to accept that only the principal factor affecting intensity, such as a matrix element for electric dipolar moment for a typical band in absorption or emission or electric dipolar polarizability for a typical band observed through Raman scattering, is a significant influence, and further contributions related to adiabatic or nonadiabatic effects – or even magnetic dipolar or electric quadrupolar contributions – must perforce be neglected during reduction of experimental data. Measurements of frequency shifts on application of external electric or magnetic field, relying on a Stark or Zeeman effect, might attain greater precision, likely $\sim 10^{-4}$ at best; as these measurements generally imply a difference between two expectation values for the involved states, they might be less sensitive to a desired property than a matrix element directly proportional to that property. In such cases there prevails consequently little or no need for a refined treatment of experimental data to encompass extra-mechanical effects or theoretical quantities representing other than a smallest order of approximation.

That effective hamiltonian according to formula 29, with neglect of $V''(R)$, appears to be the most comprehensive and practical currently available for spectral reduction when one seeks to take into account all three principal extra-mechanical terms, namely radial functions for rotational and vibrational g factors and adiabatic corrections. The form of this effective hamiltonian differs slightly from that used by van Vleck [9], who failed to recognise a connection between the electronic contribution to the rotational g factor and rotational nonadiabatic terms [150,56]. There exists nevertheless a clear evolution from the advance in van Vleck's [9] elaboration of Dunham's [5] innovative derivation of vibration-rotational energies into the present effective hamiltonian in formula 29 through the work of Herman [60,66]. The notation g for two radial functions pertaining to extra-mechanical effects in formula 29 alludes to that connection between nonadiabatic rotational effects and the magnetogyric ratio [56] that applies directly to the rotational g factor; the vibrational g factor in a product with linear momentum squared shares a similar designation [60] despite the lack of known magnetic effect. If a need arise to include effects of $V''(R)$ in formula 29, there appears also to be a direct mechanism to extend its applicability in the following way: for all contributions to $V''(R)$ that have as factor the same dependence, relative to $V(R)$, on a ratio $(m_e/m)^2$ of electronic and nuclear mass of individual atomic centres, the algebraic form of contributions to $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$ would have exactly the same form as those from $V'(R)$, through truncated polynomials analogous to those in formula 47. (Further contributions within $V''(R)$ with dependence on m_e/m to greater than second power would naturally continue to be negligible.) Any values of fitted coefficients in such polynomials would inevitably contain, besides the additional nonadiabatic effects formally in $V''(R)$, contributions propagated from approximations involving use of atomic mass rather than nuclear mass in relation to $g_r(R)$, $g_v(R)$ and $V'(R)$; the relative magnitudes of these contributions and of $V''(R)$ therein are difficult to predict. If concern about a relation between fitted parameters and particular terms within an effective hamiltonian be lacking, an alternative formulation [151] is likely practical. This hamiltonian is based on Watson's effective hamiltonian [152], in which, in a derivation towards its ultimate form, a term related to the rotational g factor at R_e is set to zero; a use [90] of such a formulation as a basis to argue that one can not deduce reliable estimates of electric dipolar moment and rotational g factor from spectra without further information from either application of external fields or theoretically calculated data is questionable. As the existence of the rotational g factor through both experiment and a theoretical basis [56] was appreciated long before Watson's derivation [152], its neglect in that derivation is a serious deficiency and an impediment to realistic application of that hamiltonian. A justification of setting equal to zero that term related to $g_r(R_e)$ is spurious, as such a criterion is both arbitrary and avoidable, as demonstrated in an alternative derivation for the same objective [72]. With the ready availability of both many experimental and calculated data for the rotational g factor [56] and computer programs to undertake such a calculation, use of Watson's hamiltonian should be avoided if one seeks to deduce from spectra a value of R_e maximally independent of atomic mass. Application of Watson's postulate [152] of a reduced mass for a diatomic molecular ion that is inconsistent in having a mass of an atomic ion in the denominator but masses of only neutral atoms in the numerator should likewise be eschewed [66]; the g factors, vibrational and rotational, properly encompass such effects for ions. Either the hamiltonian in formula 29 or an approximate variant [66] are preferable for practical application in reduction of diatomic spectral data.

In our account here we neglect a third aspect of a spectral line, specifically its shape, beyond its characteristic frequency and strength. A natural line shape is almost impracticable to observe and would yield on analysis little or no additional information about intrinsic molecular properties. Another shape merely reflects components of molecular velocities in a direction parallel to the direction of propagation. Apart from these effects, further broadening of spectral lines due to finite durations, between collisions, of molecules in particular quantum states is attributed to interactions between colliding molecules rather than directly to intrinsic molecular properties of an absorbing or emitting molecule of interest. Analysis of such effects involving multiple oscillators is not only much more complicated than a treatment of a single anharmonic oscillator from a theoretical point of view that lends itself to definition of characteristic parameters useful in fitting spectra, but has also received much less attention from a theoretical or computational point of view. A relation between terms in an effective hamiltonian for a system of only two diatomic molecules interacting during a collision and observable effects of broadening of spectral lines and modification of the shape of those lines is indirect, involving averages over several angular variables and over time. Discussion of general aspects of these collisional effects appears elsewhere [13].

A notable development since at least 1994 in relation to an application of Dunham's formalism in practical spectral analysis is a significant interplay between quantum chemistry, in a form of sophisticated calculations of molecular electronic structure and properties, and spectral reduction. In a few cases it has proved practicable to deduce information about electric and magnetic properties of diatomic molecules directly from spectral analysis through application of Dunham's formalism and its extensions, such as a significant estimate of the rotational *g* factor of GaH [89] already mentioned. In another instance, estimates of electric dipolar moment and rotational *g* factor of GeS relied upon an assumption, justified above, that adiabatic corrections are less important than nonadiabatic effects in relation to moderately massive atomic centres [153]. In these cases no assistance to spectral analysis from quantum-chemical calculations arose. In other cases [13] and likely a more typical situation, results for the radial dependence of the rotational *g* factor and adiabatic corrections have been incorporated within the reduction of spectral data of frequency type, enabling evaluation of spectral parameters of maximal quasi-physical significance – within a context of a traditional notion of molecular structure and its attendant hamiltonian; both LiH, the first application [112] of this approach, and H_2, as discussed above, are significant examples of successful derivation of information about adiabatic corrections and the vibrational *g* factor following an imposition of information about the rotational *g* factor during fitting of frequency data. For H_2 also, an imposition of information involving adiabatic corrections enabled recovery of information from experiments without externally applied electric or magnetic field about the rotational *g* factor. Although calculation of adiabatic corrections was accomplished many years ago, for instance by Kolos and Wolniewicz [108] for H_2 in 1964 through calculations of a nature specific for that molecular target, a general approach to calculation of the rotational *g* factor required further decades before suitable methods became developed; the first calculation involved direct sums of electronic matrix elements over electronic states [154], but a refined method, more practical for molecules containing many electrons, involving a polarization propagator [155], ensued a few years subsequently. A practical algorithm for calculation of the vibrational *g* factor has subsequently been devised [107,108]. With an incorporation of computer code required for all three extra-mechanical properties into computer program *Dalton* [156] for general calculations of molecular electronic structure and properties, it will have become practical to supplement point-wise calculations of a radial function for potential energy, with basis sets of great quality and taking into account electronic correlation, with these auxiliary influences on vibration-rotational energies; one can hence calculate the wave number of such a transition almost within the accuracy of typical superior measurements. Likewise one can calculate influences on intensities of transitions, such as not only the principal factors of electric dipolar moment or electric dipolar polarizability but also magnetic dipolar and electric quadrupolar moments; this information can much assist the search for further transitions for known carriers of a vibration-rotational spectrum or new transitions of uncommon species.

The result of this interaction between quantum chemistry, through methods to calculate molecular electronic structure, of not merely gross determinants of spectral features but even intimate details marks the emergence of an approach to conduct of scientific research properly termed *computational spectrometry*. Although calculations of electric dipolar moments of molecules have been practised essentially since the earliest years after the evolution of quantum mechanics in forms of wave mechanics and matrix mechanics, typical results pertained to only a single internuclear distance, generally at or near a known R_e, so equivalent to p_0; such a value pertains to the intensity of the pure rotational band but not to vibration-rotational bands that are generally more readily measurable. Early solutions for prototypical systems, including an anharmonic oscillator by Heisenberg in his original treatment [157] that became matrix mechanics and a rigid rotor by Dennison whose treatment according to matrix mechanics [158] during work in Bohr's institute in Copenhagen preceded Schrodinger's treatment of a rotating harmonic oscillator according to wave mechanics [159], continue indeed to serve, with Bohr's [160] and Schrodinger's [161] treatments of the H atom, as standard simple models for the interpretation of gross features of atomic and molecular spectra. Even though radial functions for potential energy were also calculated early, with typically only qualitatively correct results, practical methods of calculating minor but significant contributions to discrete energies of molecular states have been developed much more recently. The principal factor governing the intensity of vibration-rotational transitions observed in Raman scattering is the electric dipolar polarizability; unlike the static polarizability, for which some early calculations were made, the dynamic polarizability [162,163], which is dependent on the frequency of excitation of the Raman scattering and which is consequently required to produce an accurate comparison with or prediction for experiment, was a more recent target of accurate calculations. As remarked above, measurement of intensities of typical vibration-rotational and pure rotational spectra in absorption and emission and in Raman scattering, whether by spontaneous or coherent mechanisms [13], yields only modest accuracy, and hence requires only the dominant factors of electric dipolar moment and polarizability quantities to be calculated, nevertheless accurately, as a function of internuclear distance for an adequate theoretical description or computational prediction of these spectral properties. In contrast the great accuracy of measurement of wave number of radiation, or energy of photons, corresponding to differences between spectral terms, or energies, of vibration-rotational states, requires not only sophisticated calculation of radial functions for potential energy but also for rotational and vibrational g factors and adiabatic corrections. With the accomplishment of the latter capabilities in standard software one can consider computational spectrometry to have attained a mature state. As a basis of application of Dunham's algebraic formulation, the effective hamiltonian in formula 29 is clearly well suited to the practice of computational spectrometry because a direct relation exists between terms in this hamiltonian and quantities readily subject to theoretical calculation [66]. In principle, even the generator-coordinate approach [74,75] constitutes a mechanism for computational spectrometry still conforming to the Dunham formulation because it is expected to be able to encompass intrinsically [164] what are regarded as supplementary adiabatic and nonadiabatic corrections to molecular energies according to a traditional separation of electronic and nuclear motions. The rotational g factor seems to have been ignored in the development of that generator-coordinate approach, despite a well founded connection of g_r to both experimental and theoretical quantities; because g_r is just as much an experimentally observable quantity, through the Zeeman effect, as a wave number of a spectral line, this property warrants attention if the generator-coordinate approach is to be considered a serious means to interpret molecular spectra.

11. CONCLUSION

Dunham's expression in formula 8 for vibration-rotational terms is a double expansion in vibrational and rotational quantum numbers based on the minimum vibration-rotational energy in a particular electronic state; likewise his radial function for internuclear potential energy $V(x)$, in formula 16, which serves as a basis to relate Dunham coefficients Y_{kl}, is an expansion about the minimum potential energy of that electronic state, which occurs at the equilibrium internuclear separation R_e: both expansions thus possess the disadvantages from which all such truncated power series suffer. This property of a limited range of convergence hence bestows emphasis on vibrational states with small values of quantum number v – those states that with their associated rotational states typically pertain to almost all measurements of infrared and Raman spectra of gaseous substances containing diatomic molecular species, and even to many electronic spectra of such samples in absorption. An alternative general formula for vibration-rotational terms encompassing all states within a manifold up to a dissociation limit has never been devised [13]. The exponentially increasing extent of expressions for coefficients Y_{kl}, despite a powerful implementation of symbolic software to their elucidation [44], with increasing terms or parameters in $V(x)$, and associated functions, remains a formal impediment to enhanced application according to a theory based on an algebraic approach of Dunham and his successors, although in practice a limiting condition has seldom if ever arisen.

An important fact underlying this approach to analysis of molecular spectra based on a formalism arising from pioneering work of Dunham and van Vleck, and advances contributed by their successors, or any other approach, is that not merely coefficients A^{i}_{kl}, $V^{a,b}_{kl}$, $\Delta^{a,b}_{kl}$, B_{kl} or their equivalents but also Y^{i}_{kl}, various Z^{i}_{kl}, U_{kl}, radial coefficients a_j, c_j, p_j, s_j, t_j, u_j or their equivalent, and even R_e and k_e, or fitted values that nominally represent prospective integral kernels in expressions for Y_{kl}^{GCA} according to the generator-coordinate theory [74,75], are, first and foremost, merely *fitting parameters*; their particular numerical values adopted according to a given fitting procedure reflect both the quality and quantity of fitted data through extents both of ranges of vibrational and rotational quantum numbers and of isotopic variants, as exemplified through results for NaCl described above. Apart from representatives of integral kernels, the coefficients $a_j \ldots u_j$ listed above pertain to radial functions that are artifacts of a method of separate treatment of electronic and nuclear motions; those radial functions, such as of potential energy or electric dipolar moment, are not experimentally observable, even though they might be susceptible to calculation according to some ansatz. Some fitting parameters of one or other type might be more suitable to use for moderate extrapolation beyond those extents of data than parameters of other types if a theoretically justified fitting model be chosen, but any such extrapolation is fundamentally statistically unreliable and susceptible to propagation of error associated with the original experimental measurements, even if limiting forms or conditions be imposed on the fitting formula; the reliability or accuracy invariably decreases with an increasing extent of extrapolation beyond characterised states of molecular energies. Although some parameters of selected type according to a selected model might be amenable to comparison with quantities calculated theoretically, the latter calculations involve both approximate models and approximations in implementation that proscribe an exact comparison, because any diatomic molecule must involve interaction of at least three elementary particles for which the problem of *many bodies* fundamentally lacks an exact solution. Nevertheless, a nominally theoretical – actually still *semi-empirical* in practice – calculation of pertinent quantities can beneficially guide experimental measurements; conversely, experimental measurements can guide development of theories, as has occurred repeatedly since the first measurements of optical spectra. Of course any ansatz of purported calculation from first principles or *ab initio* reflects, implicitly, prior experimental information and influence. The development of molecular spectrometry represents a prime confluence of theory, experiment and computation – the latter through methods of quantum chemistry, and has afforded many implications for our understanding of myriad chemical and physical phenomena. An approach to a quantitative description of spectra of diatomic molecular species through Dunham's systematic algebraic formalism, based naturally on Dunham coefficients Y_{kl}, has served as a model for an area of science much broader than the number of atomic centres in a molecule of a size that attracted his attention might indicate.

ACKNOWLEDGEMENTS

We thank Dr. S.P.A. Sauer of University of Copenhagen for fruitful collaboration in a project since 1994 of which this article is an overview, and Professor P. van Leuven for helpful comments about the generator coordinate approach. Much preparation of this article occurred whilst JFO was a visiting professor in Kemisk Institut at Syddansk Universitet, for which hospitality he is grateful.

REFERENCES

[1] J. L. Dunham, *Phys. Rev.*, 1929, **34**, 438.
[2] J. L. Dunham, *Phys. Rev.*, 1930, **35**, 1347.
[3] J. L. Dunham, *Phys. Rev.*, 1930, **36**, 1553.
[4] J. L. Dunham, *Phys. Rev.*, 1932, **41**, 713.
[5] J. L. Dunham, *Phys. Rev.*, 1932, **41**, 721.
[6] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2nd edn, van Nostrand, New York, 1950.
[7] Science Citation Index, 2004.
[8] H. C. Urey, G. M. Murphy and F. G. Brickwedde, *Phys. Rev.*, 1932, **40**, 1.
[9] J. H. van Vleck, *J. Chem. Phys.*, 1936, **4**, 327.
[10] J. J. Balmer, *Ann. Phys. Chem.*, 1885, **25**, 80.
[11] H. Deslandres, *Comptes Rendus Acad. Sci. Paris*, 1886, **103**, 972.
[12] M. M. Hessel and C. R. Vidal, *J. Chem. Phys.*, 1979, **70**, 4439.
[13] J. F. Ogilvie, *The Vibrational and Rotational Spectrometry of Diatomic Molecules*, Academic Press, London, 1998, and references therein.
[14] L. Brillouin, *Comptes Rendus Acad. Sci. Paris*, 1926, **183**, 24, and 270.
[15] L. Brillouin, *J. Phys. Radium*, 1926, **7**, 136, and 353.
[16] H. A. Kramers, *Z. Phys.*, 1926, **39**, 828.
[17] G. Wentzel, *Z. Phys.*, 1926, **38**, 518.
[18] H. Jeffreys, *Proc. London Math. Soc.*, 1925, **23**, 428.
[19] I. Sandeman, *Proc. R. Soc. Edinburgh*, 1940, **60**, 210.
[20] (a) H. W. Woolley, *J. Chem. Phys.*, 1962, **37**, 1307; (b) H. W. Woolley, *J. Chem. Phys.*, 1972, **56**, 1792.
[21] J. E. Kilpatrick, *J. Chem. Phys.*, 1959, **30**, 801.
[22] J. P. Bouanich, *J. Quant. Spectrosc. Radiat. Transfer*, 1978, **19**, 381.
[23] V. N. Brukhanov, V. Y. Galin, V. E. Zuev, Y. S. Makushkin and V. G. Tyuterev, *Opt. Spectrosc.*, 1982, **52**, 33.
[24] N. Bessis, G. Hadinger and Y. S. Tergiman, *J. Mol. Spectrosc.*, 1984, **107**, 343.
[25] G. Hadinger, Y. S. Tergiman and G. J. Hadinger, *J. Chem. Phys.*, 1987, **87**, 2143.
[26] J. F. Ogilvie and R. H. Tipping, *Int. Rev. Phys. Chem.*, 1983, **3**, 3.
[27] J. F. Ogilvie and M. B. Monagan, *MapleTech*, 1997, **4**, 100.
[28] H. Uehara, *J. Mol. Spectrosc.*, 1998, **188**, 215.
[29] H. Uehara, K. Horiai and K. Akiyama, *Bull. Chem. Soc. Jpn*, 2004, **77**, xxx–xxx.
[30] F. M. Fernandez and J. F. Ogilvie, *Phys. Rev. A*, 1990, **42**, 4001.
[31] M. B. Monagan and J. F. Ogilvie, *Math. Comput. Simulat.*, 1999, **49**, 221.
[32] R. H. Tipping, *J. Mol. Spectrosc.*, 1972, **43**, 31.
[33] R. H. Tipping and J. F. Ogilvie, *Chin. J. Phys.*, 1990, **28**, 237.
[34] J. F. Ogilvie and D. Koo, *J. Mol. Spectrosc.*, 1976, **61**, 332.
[35] A. H. M. Ross, R. S. Eng and H. Kildal, *Opt. Commun.*, 1974, **12**, 433.
[36] C. M. Clayton, D. W. Merdes, J. Pliva, T. K. McCubbin and R. H. Tipping, *J. Mol. Spectrosc.*, 1983, **98**, 168.
[37] P. Niay, P. Bernage, C. Coquant and A. Fayt, *Can. J. Phys.*, 1977, **55**, 1829.
[38] G. Simons, R. G. Parr and J. M. Finlan, *J. Chem. Phys.*, 1973, **59**, 3229.
[39] A. Kratzer, *Z. Phys.*, 1920, **3**, 289.
[40] E. Fues, *Ann. Phys.*, 1926, **80**, 367.
[41] (a) J. F. Ogilvie, *Proc. R. Soc. London*, 1981, **A378**, 287; (b) J. F. Ogilvie, *Proc. R. Soc. London*, 1982, **A381**, 479, and references therein.
[42] C. L. Beckel, *J. Chem. Phys.*, 1976, **65**, 4319.
[43] J. F. Ogilvie, *Comput. Phys. Commun.*, 1983, **30**, 101.
[44] F. M. Fernandez and J. F. Ogilvie, *MapleTech*, 1998, **5**, 42.
[45] E. Tiemann, H. Knockel and J. Schlembach, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 821.
[46] N. Bohr, *Nature*, 1922, **109**, 746.
[47] W. H. King, *Isotope Shifts in Atomic Spectra*, Plenum Press, London, 1984.

[48] P. Brix and H. Kopfermann, *Z. Phys.*, 1949, **126**, 344.
[49] J. Schlembach and E. Tiemann, *Chem. Phys.*, 1982, **68**, 21.
[50] P. Aufmuth, K. Heilig and A. Steudel, *At. Data Nucl. Data Tables*, 1987, **37**, 455.
[51] G. Fricke, C. Bernhardt, K. Heilig, L. A. Schaller, L. Schellenberg, E. B. Shera and C. W. de Jager, *At. Data Nucl. Data Tables*, 1995, **60**, 177.
[52] C. Wieman and T. W. Hansch, *Phys. Rev. A*, 1980, **22**, 192.
[53] G. W. Erickson, *J. Phys. Chem. Ref. Data*, 1977, **6**, 831.
[54] (a) R. M. Herman and S. Short, *J. Chem. Phys.*, 1968, **48**, 1266; (b) R. M. Herman and S. Short, *J. Chem. Phys.*, 1970, **50**, 572.
[55] J. F. Ogilvie, *J. Phys. At. Mol. Opt. Phys. B*, 1994, **27**, 47.
[56] J. F. Ogilvie, J. Oddershede and S. P. A. Sauer, *Adv. Chem. Phys.*, 2000, **111**, 475, and references therein.
[57] J. Korving, H. Hulsman, L. J. F. Hermans, J. J. de Groot, H. F. P. Knapp and J. J. M. Beenakker, *J. Mol. Spectrosc.*, 1966, **20**, 294.
[58] L. J. F. Hermans, A. Schutte, H. F. P. Knapp and J. J. M. Beenakker, *Physica*, 1970, **46**, 491.
[59] H. Moraal and F. R. McCourt, *Phys. Rev. A*, 1971, **4**, 511.
[60] R. M. Herman and A. Asgharian, *J. Mol. Spectrosc.*, 1966, **19**, 305.
[61] M. Born and J. R. Oppenheimer, *Ann. Phys. Leipzig*, 1927, **84**, 457.
[62] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford, 1954.
[63] H. C. Longuet-Higgins, *Adv. Spectrosc.*, 1961, **2**, 263.
[64] F. M. Fernandez, *Phys. Rev.*, 1994, **50**, 2953.
[65] R. G. Woolley, *Adv. Phys.*, 1976, **25**, 27.
[66] R. M. Herman and J. F. Ogilvie, *Adv. Chem. Phys.*, 1998, **103**, 187.
[67] P. R. Bunker and R. E. Moss, *Mol. Phys.*, 1977, **33**, 417.
[68] W. C. Stwalley, *J. Chem. Phys.*, 1975, **63**, 3062.
[69] E. Tiemann and J. F. Ogilvie, *J. Mol. Spectrosc.*, 1994, **165**, 377.
[70] J. F. Ogilvie, *J. Mol. Spectrosc.*, 1996, **180**, 193.
[71] J. F. Ogilvie, *Spectrosc. Lett.*, 1989, **22**, 477.
[72] F. M. Fernandez and J. F. Ogilvie, *Chin. J. Phys.*, 1992, **30**, 177, and 599.
[73] M. R. Osborne, *J. Aust. Math. Soc. B*, 1976, **19**, 343.
[74] L. Lathouwers and P. van Leuven, *Adv. Chem. Phys.*, 1982, **49**, 115.
[75] L. Lathouwers, P. van Leuven, E. Deumens and Y. Ohrn, *J. Chem. Phys.*, 1987, **86**, 6352.
[76] G. Poeschl and E. Teller, *Z. Phys.*, 1933, **83**, 143.
[77] R. Engelke, *Am. J. Phys.*, 1989, **57**, 339.
[78] M. M. Nieto, *Phys. Rev. D*, 1981, **24**, 1030.
[79] I. M. Gelfand and B. M. Levitan, *Izv. Akad. Nauk USSR, Math. Ser.*, 1951, **15**, 309.
[80] (a) A. G. Ramm, *Inv. Prob.*, 1988, **4**, 877; (b) A. G. Ramm, *Inv. Prob.*, 1988, **5**, 255.
[81] J. F. Ogilvie, H. Uehara and K. Horiai, *Bull. Chem. Soc. Jpn*, 2000, **73**, 321.
[82] J. F. Ogilvie, H. Uehara and K. Horiai, *Can. J. Anal. Sci. Spectrosc.*, 1999, **44**, 141.
[83] F. M. Fernandez and J. F. Ogilvie, *J. Math. Chem.*, 1994, **15**, 131.
[84] F. M. Fernandez, *J. Math. Phys.*, 1995, **36**, 3922, and references therein.
[85] H. Uehara and J. F. Ogilvie, *J. Mol. Spectrosc.*, 2001, **207**, 143.
[86] Q. J. Hu, T. C. Melville and J. W. Hepburn, *J. Chem. Phys.*, 2003, **119**, 8938.
[87] N. C. Handy and A. M. Lee, *Chem. Phys. Lett.*, 1996, **252**, 425.
[88] J. F. Ogilvie, *Chem. Phys. Lett.*, 1997, **267**, 590.
[89] J. F. Ogilvie and S. C. Liao, *Chem. Phys. Lett.*, 1994, **226**, 281.
[90] J. K. G. Watson, *J. Mol. Spectrosc.*, 2003, **217**, 157.
[91] R. D. Urban, H. Birk, P. Polomsky and H. Jones, *Chem. Phys. Lett.*, 1989, **154**, 135.
[92] R. D. Urban, H. Birk, P. Polomsky and H. Jones, *J. Chem. Phys.*, 1991, **94**, 2523.
[93] J. M. Campbell, M. Dulick, D. Klapstein, J. B. White and P. F. Bernath, *J. Chem. Phys.*, 1993, **99**, 8379.
[94] P. J. Mohr and B. N. Taylor, *Rev. Mod. Phys.*, 2005, **77**, 1.
[95] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules*, van Nostrand-Reinhold, New York, 1979.
[96] S. P. A. Sauer, J. Oddershede and J. Geertsen, *Mol. Phys.*, 1992, **76**, 445.

[97] S. P. A. Sauer and J. F. Ogilvie, *J. Phys. Chem.*, 1994, **98**, 8617.
[98] S. P. A. Sauer, *Chem. Phys. Lett.*, 1996, **260**, 271.
[99] J. F. Ogilvie, S.-L. Cheah, Y.-P. Lee and S. P. A. Sauer, *Theor. Chem. Acc.*, 2002, **108**, 85.
[100] S. R. Langhoff, C. W. Baushlicher and H. Partridge, *Chem. Phys. Lett.*, 1994, **223**, 416.
[101] J. F. Ogilvie, *Chem. Phys. Lett.*, 1992, **191**, 592.
[102] P. M. Morse, *Phys. Rev.*, 1929, **34**, 57.
[103] J. F. Ogilvie, *J. Chem. Phys.*, 1988, **88**, 2804.
[104] J. F. Ogilvie, *Can. J. Spectrosc.*, 1988, **33**, 72.
[105] M. L. Orlov, J. F. Ogilvie and J. W. Nibler, *J. Mol. Spectrosc.*, 1997, **185**, 128.
[106] I. Dabrowski, *Can. J. Phys.*, 1984, **62**, 1639.
[107] K. L. Bak, S. P. A. Sauer, J. Oddershede and J. F. Ogilvie, *Ohio State Univ. Int. Symp. Mol. Spectrosc.*, 2003, **58**, Abstract FD02.
[108] K. L. Bak, S. P. A. Sauer, J. Oddershede and J. F. Ogilvie, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1747.
[109] S.P.A. Sauer, J. Oddershede, J.F. Ogilvie, Evaluation of parameters in radial functions from rotational and vibration–rotational spectra and calculation of rotational and vibrational g factors for LiH $X^1\Sigma^+$, in preparation.
[110] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1964, **41**, 3663.
[111] L. Wolniewicz, *J. Chem. Phys.*, 1993, **99**, 1851.
[112] R. G. Barnes, P. J. Bray and N. F. Ramsey, *Phys. Rev.*, 1954, **94**, 893.
[113] J. D. Garcia, *Phys. Rev.*, 1966, **147**, 66.
[114] J. F. Ogilvie, J. Oddershede and S. P. A. Sauer, *Chem. Phys. Lett.*, 1994, **228**, 183.
[115] R. R. Freeman, A. R. Jacobson, D. W. Johnson and N. F. Ramsey, *J. Chem. Phys.*, 1975, **63**, 2597.
[116] T. R. Lawrence, C. H. Anderson and N. F. Ramsey, *Phys. Rev.*, 1963, **130**, 1865.
[117] M. Dulick, K.-Q. Zhang, B. Guo and P. F. Bernath, *J. Mol. Spectrosc.*, 1998, **188**, 14.
[118] E. F. Pearson and W. Gordy, *Phys. Rev.*, 1969, **177**, 59.
[119] G. M. Plummer, E. Herbst and F. C. de Lucia, *J. Chem. Phys.*, 1984, **81**, 4893.
[120] F. Matsushima, H. Odashima, D. B. Wang, S. Tsunekawa and K. Takagi, *Jpn. J. Appl. Phys.*, 1994, **33**, 315.
[121] M. Bellini, P. de Natale, M. Inguscio, T. D. Varberg and J. M. Brown, *Phys. Rev. A*, 1995, **52**, 1954.
[122] D. M. Bishop and L. M. Cheung, *J. Chem. Phys.*, 1983, **78**, 1396.
[123] C. E. Scheu, D. B. Kinghom and L. Adamowicz, *J. Chem. Phys.*, 2001, **114**, 3393.
[124] M. Cafiero, S. Bubin and L. Adamowicz, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1491.
[125] H. Partridge and S. R. Langhoff, *J. Chem. Phys.*, 1981, **74**, 2361.
[126] W. C. Stwalley and W. T. Zemke, *J. Phys. Chem. Ref. Data*, 1993, **22**, 87.
[127] J. F. Ogilvie, *Cryst. Eng.*, 2004, **6**, 255.
[128] C. P. Smyth, *Philos. Mag.*, 1923, **45**, 849.
[129] J. F. Ogilvie and Y. P. Lee, *Chem. Phys. Lett.*, 1989, **159**, 239.
[130] R. Herman and R. F. Wallis, *J. Chem. Phys.*, 1955, **23**, 637.
[131] J. N. P. van Stralen, L. Visscher and J. F. Ogilvie, *Chem. Phys. Phys. Chem.*, 2004, **6**, 3779.
[132] R. Beck, W. Englisch and K. Gurs, *Table of Laser Lines in Gases and Vapours*, 3rd edn, Springer, Berlin, 1980.
[133] M. Gromoll-Bohle, W. Bohle and W. Urban, *Opt. Commun.*, 1989, **69**, 409.
[134] G. Guelachvili, D. de Villeneuve, R. Farrenq, W. Urban and J. Verges, *J. Mol. Spectrosc.*, 1983, **98**, 64.
[135] K. Angstrom, *Ofvers. Kongl. Vet. Akad. Forh. Stockholm*, 1889, **46**, 203.
[136] G. Herzberg and K. N. Rao, *J. Chem. Phys.*, 1949, **17**, 1099.
[137] C.-Y. Chung, Y.-P. Lee, J. F. Ogilvie, to be published, 2005.
[138] A. O'Keefe and D. A. G. Deacon, *Rev. Sci. Instrum.*, 1988, **59**, 2544.
[139] J. S. Muenter, *J. Mol. Spectrosc.*, 1975, **55**, 490.
[140] J. F. Ogilvie, *Chem. Comput.*, 1984, **8**, 205.
[141] C. Chackerian and R. H. Tipping, *J. Mol. Spectrosc.*, 1983, **99**, 431.
[142] Y.-P. Lee, S.-L. Cheah and J. F. Ogilvie, *Infrared Phys. Tech.*, 2005, **46**, in press.
[143] J. F. Ogilvie and M. Molski, *Spectrochim. Acta A*, 1999, **55**, 1427, and references therein.

[144] J. F. Ogilvie, *Chem. Phys. Lett.*, 2001, **348**, 447, and references therein.
[145] G. Audi, A. H. Wapstra and C. Thibault, *Nucl. Phys. A*, 2003, **729**, 337.
[146] S. Saupe, B. Meyer, M. H. Wappelhorst, W. Urban and A. G. Maki, *J. Mol. Spectrosc.*, 1996, **179**, 13.
[147] F. Lewen, S. Brunken, G. Winnewisser, M. Simeckova and S. Urban, *J. Mol. Spectrosc.*, 2004, **226**, 113.
[148] S. Klee and J. F. Ogilvie, *Spectrochim. Acta A*, 1993, **49**, 345.
[149] M. Caris, F. Lewen and G. Winnewisser, *Z. Naturforsch*, 2002, **57a**, 663.
[150] B. Rosenblum, A. H. Nethercot and C. H. Townes, *Phys. Rev.*, 1958, **109**, 400.
[151] H. Uehara, K. Horiai and K. Akiyama, *Bull. Chem. Soc. Jpn*, 2004, **77**, 1821.
[152] J. K. G. Watson, *J. Mol. Spectrosc.*, 1980, **80**, 411.
[153] J. F. Ogilvie, *Mol. Phys.*, 1996, **88**, 1055.
[154] D. M. Bishop and L. M. Cheung, *J. Chem. Phys.*, 1981, **74**, 1817.
[155] J. Oddershede and J. R. Sabin, *Chem. Phys.*, 1988, **122**, 291.
[156] Dalton, a molecular–electronic–structure program, release 2.0 (2004), written by T. Helgaker, H. J.Aa. Jensen, P. Joergensen, J. Olsen, K. Ruud, H. Aagren, A. A. Auer, K. L. Bak, V. Bakken, O. Christiansen, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Hattig, K. Hald, A. Halkier, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. B. Pedersen, T. A. Ruden, A. Sanchez, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras; on Internet, http://www.kjemi.uio.no/software/dalton/dalton.html
[157] W. Heisenberg, *Z. Phys.*, 1925, **33**, 879.
[158] D. M. Dennison, *Phys. Rev.*, 1926, **28**, 318.
[159] E. Schrodinger, *Ann. Phys. Leipzig*, 1926, **79**, 489.
[160] N. Bohr, *Philos. Mag.*, 1913, **26**, 1.
[161] E. Schrodinger, *Ann. Phys. Leipzig*, 1926, **79**, 361.
[162] J. Oddershede, P. Joergensen and N. H. F. Beebe, *J. Chem. Phys.*, 1975, **63**, 2996.
[163] J. Oddershede and E. N. Svendsen, *Chem. Phys.*, 1982, **64**, 359.
[164] L. Lathouwers and P. van Leuven, *Chem. Phys. Lett.*, 1980, **70** , 410.