The Spirits of Mendeleyev and Dunham in the Analysis of Molecular Spectra

Application of Symbolic Computation to Derivation of an Algorithm to Evaluate Quantitatively the Potential Energy, Adiabatic and Nonadiabatic and other Properties of Diatomic Molecules

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ABSTRACT

After deriving the effective hamiltonian for the motion of the nuclei in the field of the electrons, including terms for the adiabatic and nonadiabatic effects arising from the imperfect following by the electrons of the nuclear vibrations and rotations, we use symbolic computation in the spirit of Dunham to obtain analytic relations for the term coefficients as functions of the parameters in the radial functions in the effective hamiltonian. The resulting terms include explicitly the proper dependence on the atomic reduced mass and on the mass of individual nuclei so that the values of the parameters are entirely independent of the effects of nuclear mass, in the spirit of Mendeleyev. Applications of this formalism to HCl and other molecules for which abundant vibration-rotational spectra are available illustrate the orders of magnitudes of the various coefficients and the accuracy of the computational approach.

1. INTRODUCTION

To chemists and physicists Dmitri Ivanovich Mendeleyev (1834-1907), born in Tobolsk in Siberia, needs no introduction. His greatest contribution to the development of science was his recognition that classification of chemical elements should be based on atomic number, not atomic mass. In its still evolving form, the modern periodic chart that will be forever linked with Mendeleyev's name is based immutably upon the principle that not only the most important physical properties of the elements but also the nature of their compounds depend primarily upon the number of protons in the atomic nucleus, and far secondarily upon the number of neutrons that with the atomic number determines the atomic mass.

Born in New York City U.S.A., James Lawrence Dunham (1904-1933) passed most of his academic life at Harvard University in Boston U.S.A. Before his untimely death as the result of unsuccessful surgery, he was primarily a theoretical physicist who made significant *contributions in the field of wave mechanics*. In 1932 Dunham published two papers that have since maintained major impact upon the development of physics and molecular spectroscopy of diatomic molecules. First Dunham outlined the then new JBKW technique that has become a staple method for the solution of one-dimensional problems in physics.[1] Then Dunham applied this JBKW technique to the rotating vibrator according to an analytic approach that led to expressions for the energy coefficients Y_{kl} in terms of parameters in the radial function for potential energy;[2] these expressions—but especially the systematic notation—are still commonly used. As Dunham recognised, his theory failed to take directly into account the adiabatic and nonadiabatic effects that lead to deviations of mass scaling of these term coefficients. Because of relentlessly increasing spectral resolution, the correspondingly precise measurement of spectral lines—$\delta\nu/\nu \sim 10^{-9}$ in the best cases, and availability of spectra of isotopic variants that may consist of thousands of assigned lines, that exhibit these mass effects, spectral data of the present quality and quantity far surpass theoretical description within the confines of Dunham's theory. In the sense that we have during the course of the present work produced a quantitative description of these effects in terms of the applicable radial functions, we have been able to complete the task that Dunham initiated. The radial functions on which we base our results provide simultaneously the most compact and most physically meaningful representation of the frequencies and wavenumbers of the corresponding spectral lines.[3]

Since van Vleck's initial treatment,[4] there has been much progress in the understanding of the nature of adiabatic and nonadiabatic effects. Adiabatic effects signify that the energy of a molecule within a particular electronic state depends on not only on the internuclear distance but also the relative nuclear momenta, thus on the nuclear masses. The nonadiabatic effects arise from the failure of the electrons to follow perfectly the nuclei during their vibrational and rotational motions, and are attributed formally to interactions between the electronic state of interest, typically the electronic ground state for purposes of vibration-rotational spectroscopy, and other electronic states. Vibrational nonadiabatic effects are associated with vibrational motion of the nuclei that is supposed to induce interactions between electronic states of the same electronic angular momentum, whereas rotational motion analogously gives rise to rotational nonadiabatic effects associated with interactions between electronic states of net electronic angular momenta differing by one unit.[4] All these effects arise from the approximate separation of electronic and nuclear motions by which means Born and Oppenheimer introduced the idea of molecular structure into quantum mechanics.[5] If the energies of the vibrational and rotational states in the electronic state of interest are sufficiently distant from those in other electronic states, the interactions are sufficiently small to be considered weak and homogeneous perturbations; then the dependence on internuclear distance of these effects may be formally defined analogously to the potential energy that is the dominant factor determining the vibrational and rotational energies of the eigenstates belonging to the particular isolated electronic state. According to an analytic approach entirely in the spirit of Dunham's work, we present a formalism by which means we separate purely from experimental data the various effects, and provide an instance of application to the particular molecular species HCl. In 1923 Randall recognised the importance both of the theoretical description of vibrational and rotational motions and of experimental information about HCl in particular that could serve as a test of any pertinent theory.[6]

2. ANALYTIC TREATMENT

We begin with the nonrelativistic hamiltonian of a dinuclear molecule in the electronic state $^1\Sigma$ for which there is accordingly neither net orbital nor net spin angular momentum of the set of N electrons and for which any intrinsic nuclear angular momenta are neglected,

$$\mathcal{H} = -\hbar^2/(2m_e)\sum_{j=1}^{N}\nabla_j^2 - \tfrac{1}{2}\hbar^2\sum_{l=a,b}\nabla_l^2/M_l + (4\pi\epsilon_o)^{-1}[-\sum_{j=1}^{N}\sum_{l=a,b} Z_l e^2/r_{jl} + \sum_{j=1}^{N}\sum_{k>j}^{N} e^2/r_{jk} - Z_a Z_b/R] \qquad (1)$$

in which the first two terms represent the kinetic energies of the electrons and of the nuclei respectively; the remaining terms signify the coulombic potential energies successively of attraction between the two nuclei (having atomic numbers Z_a and Z_b) and electrons and of repulsion between the electrons and between the nuclei; r_{jl} or r_{jk} is the distance between a nucleus l and an electron j or between two electrons j and k, whereas R is the instantaneous internuclear separation. As described previously[7] following Bunker and Moss and other workers[8] we derived an effective hamiltonian for the motion of the nuclei,

$$\mathcal{H}_{eff} = \frac{-\hbar^2}{2\mu}\,\frac{d}{dR}[1 + \beta(R)]\frac{d}{dR} + V_{eff} + \frac{\hbar^2}{2\mu R^2}[1 + \alpha(R)]J(J+1) \qquad (2)$$

Therein V_{eff} comprises the effective internuclear potential energy of the nonrotating molecule,

$$V_{eff} = V^{BO}(R) + V^{ad}(R) + V^{na}(R) \qquad (3)$$

containing the contributions the potential energy $V^{BO}(R)$ that is formally independent of nuclear mass,

$V^{ad}(R)$ that takes into account adiabatic effects and $V^{na}(R)$ that takes partially into account vibrational nonadiabatic effects.[8] In equation 2 the last term containing the quantum number J for the total angular momentum of the molecule represents the centrifugal effects; the function $\alpha(R)$ takes into account the rotational nonadiabatic effects, that the electrons fail to follow perfectly the nuclei as the latter rotate about the centre of molecular mass. In the term for the nuclear kinetic energy $\beta(R)$ is an analogous function for the vibrational inertia of the electrons.

Dunham assumed a radial function for the nuclear potential energy, independent of nuclear mass, to take the form of a series in the argument x to various non-negative powers,[2]

$$V^{BO}(x) = a_0 x^2 \, (1 + \sum_{j=1}^{\infty} a_j x^j) \tag{4}$$

in which the formally infinite series becomes truncated as governed according to the finite quantity of experimental data. The argument x is a reduced displacement of the instantaneous internuclear distance R from its equilibrium length R_e; $x \equiv (R - R_e)/R_e$. Because this variable is poorly behaved as $R \to \infty$, we have introduced[9] the alternative variable $z \equiv 2(R - R_e)/(R + R_e)$ that places on an equivalent basis, $z = \pm 2$, the two limits of molecular existence, namely the separate atoms as $R \to \infty$ and the united atom at $R = 0$. The potential energy that remains formally independent of mass has the same form as that Dunham used,

$$V^{BO}(z) = c_0 z^2 \, (1 + \sum_{j=1} c_j z^j) \tag{5}$$

but in this case because of the everywhere well behaved nature of z one can apply boundary conditions to make the energy approach properly the asymptotic limit $V^{BO}(z) \to \mathbf{D}_e$, the equilibrium binding energy (relative to $V^{BO} = 0$ at $z = 0$ or $R = R_e$) as $z \to 2$;[10] hence the number of coefficients c_j can be kept finite.

For a diatomic molecule consisting of two nuclei of distinct atomic numbers with the associated electrons, there are in general two radial functions for each physical effect beyond the potential energy because the nuclear masses of atoms of each atomic number influence separately the molecular energies. The effects that we must include are the adiabatic and rotational and vibrational nonadiabatic effects, corresponding to $V^{ad}(R)$, $\alpha(R)$ and $\beta(R)$ respectively; the other function $V^{na}(R)$ in equation 3 we ignore because its order in the expansion variable[5] $\kappa \equiv (m_e/M_{at})^{1/4}$ makes it negligible relative to the retained terms;[7] m_e is the electronic rest mass and M_{at} is the average atomic mass. To take into account these essential effects we introduce the following correspondences,

$$V^{ad}(R) \to (m_e/M_a) \sum_{j=1} u_j^a z^j + (m_e/M_b) \sum_{j=1} u_j^b z^j \tag{6}$$

$$\alpha(R) \to (m_e/M_a) \sum_{j=0} t_j^a z^j + (m_e/M_b) \sum_{j=0} t_j^b z^j \tag{7}$$

$$\beta(R) \to (m_e/M_a) \sum_{j=0} s_j^a z^j + (m_e/M_b) \sum_{j=0} s_j^b z^j \tag{8}$$

that define the coefficients of the pertinent radial functions. The summations begin at $j = 0$ for the latter two functions, but at $j = 1$ for the adiabatic effects because any constant term therein contributes simply to the zero-point energy taken into account elsewhere. For a diatomic molecule containing two nuclei having in each nucleus the same numbers of protons but not necessarily the same numbers of neutrons, each pair of related coefficients merges into a single coefficient having as quotient the reduced mass of the molecule instead of the individual atomic masses. We use in general the atomic masses rather than nuclear masses because the latter are relatively inaccurately known and because the consequent error is much smaller than error propagated from currently available measurements of transition frequencies. According to these definitions the magnitudes of the coefficients c_j, $j > 0$, and all $t_j^{a,b}$ and $s_j^{a,b}$ are expected to be of order unity whereas the magnitudes of c_0 and all coefficients $u_j^{a,b}$ are expected to be of order B_e/γ^2; γ is the ratio of the limiting separation $2B_e$ between adjacent rotational lines to the limiting separation ω_e between the centres of adjacent vibrational bands in a progression of an absorption spectrum; the range of values of $\gamma \equiv 2B_e/\omega_e$ is $[10^{-4}, 0.026]$ for known diatomic molecules in their electronic ground states. The expansion coefficient γ governs the rate of convergence of expressions consisting of a sequence of contributions having as factor γ to successively increasing powers; magnitudes of γ within the stated range ensure that at most a few contributions suffice to define molecular energies with accuracy comparable to that of the measurement of spectral lines.

Following Dunham[2] and the subsequent extension,[11] we express the vibration-rotational terms in the systematic form

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b})(v + ½)^k (J^2+J)^l \tag{9}$$

in which we suppress the explicit isotopic dependence of E_{vJ} and the term coefficients Y_{kl} and $Z_{kl}^{v,r}$. In this equation and elsewhere we assume hereafter that the units of all quantities E_{vJ}, Y_{kl}, Z_{kl}^{v}, Z_{kl}^{r}, the potential energy $V(z)$ and the coefficients c_0 and all $u_j^{a,b}$ are those of wavenumber, whereas the remaining coefficients c_j, $j > 0$, $t_j^{a,b}$ and $s_j^{a,b}$ are dimensionless. The term coefficients Y_{kl} depend on the molecular parameters the harmonic force coefficient k_e, the equilibrium separation R_e, the potential-energy coefficients c_j, $j > 0$, and the atomic masses through the molecular reduced mass $\mu \equiv M_a M_b/(M_a + M_b - Z_n m_e)$ in which Z_n is the net electric charge of the molecular species in units of the protonic charge, because $B_e \equiv h/(8\pi^2 c \mu R_e^2)$, $\omega_e \equiv (k_e/\mu)^{½}/(2\pi c)$ and $c_0 \equiv ½ k_e R_e^2/(hc)$. Of these term coefficients Y_{kl} we have derived expressions containing c_j up to $j = 24$, including all Y_{kl} such that $2k + l \leqslant 12$ and some important further terms up to $Y_{13,0}$, $Y_{12,1}$ etc. A few expressions appear in table 1 as examples; a larger collection containing c_j up to $j = 10$ has been published, with their derivatives with respect to the parameters, in machine-readable form,[12] and further expressions will be made available subsequently. These expressions Y_{kl} have the form

$$Y_{kl} = \sum_{m=0} Y_{kl}^{(2m)} \tag{10}$$

in which each successive contribution $Y_{kl}^{(2m)}$ contains a further factor γ^2; in practice for most combinations of the subscripts k and l only the leading term Y_{kl}^{0} provides sufficient accuracy, whereas even for the most important coefficients $Y_{1,0}$ and $Y_{0,1}$ at most only the first three contributions are required. These leading terms Y_{kl}^{0} are also expressed as the product $U_{kl}\mu^{-(½k+l)}$ of the reduced mass μ to the indicated power and the further term coefficients U_{kl} that hence become formally independent of nuclear mass. The latter coefficients are used in an alternative expression of the vibration-rotational energies,[13]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl}\mu^{-(½k+l)}[1 + m_e(\Delta_{kl}^{a}/M_a + \Delta_{kl}^{b}/M_b)](v+½)^k (J^2+J)^l \tag{11}$$

in which the additional empirical coefficients $\Delta_{kl}^{a,b}$ are supposed to take into account both $Y_{kl}^{(2m)}$ with $m > 0$ and the deviations from the mass-scaling properties of the coefficients U_{kl} arising from the various adiabatic and nonadiabatic effects in inextricable combination. The expressions in table 1 are equivalent to those that Dunham reported in terms of his coefficients a_j,[2] but our expressions involving coefficients c_j of z^j are not only more extensive but also more practical for the reason already stated.

The additional term coefficients of types Z_{kl}^{r} and Z_{kl}^{v} we assume to be experimentally distinguishable; this assumption we justify subsequently. According to our theoretical derivation, the total expressions Z_{kl} are directly partitioned on the basis of the terms in the hamiltonian that lead to their various contributions.[7] For instance the coefficients $u_j^{a,b}$ appear in only the expressions of $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$, and analogously the coefficients $t_{kl}^{a,b}$ in only $Z_{kl}^{r,a}$ and $Z_{kl}^{r,b}$, but the coefficients $s_{kl}^{a,b}$ occur in almost all $Z_{kl}^{r,a}$, $Z_{kl}^{r,b}$, $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$, as tables 2 and 3 illustrate. These coefficients $Z_{kl}^{r,v}$ hence depend on the atomic masses, the molecular parameters the harmonic force coefficient k_e, the equilibrium separation R_e, the potential-energy coefficients c_j, $j > 0$, in addition to the coefficients $u_j^{a,b}$, $t_j^{a,b}$ and $s_j^{a,b}$, all the latter in a linear manner. To produce these expressions, using hypervirial perturbation theory[14] we suppressed terms of order beyond $(m_e/M_{at})^1$ relative to their context.[7] Because direct expansion of the vibrational nonadiabatic function $\beta(R)$ in the effective hamiltonian, equation 2, gives rise to unbound contributions

Table 1. Expressions for term coefficients Y_{kl} in terms of potential-energy coefficients c_j

$$Y_{0,0} = 0 + B_e(- 7c_1^2/32 - c_1/8 + 3c_2/8 + 1/16) + \ldots$$

$$Y_{0,1} = B_e + B_e^3/\omega_e^2(21c_1^3/4 + 27c_1^2/4 - 23c_1c_2/2 + 35c_1/8 - 8c_2 + 15c_3/2 + 2) + \ldots$$

$$\begin{aligned}Y_{0,2} = {} & -4B_e^3/\omega_e^2 + B_e^5/\omega_e^4(- 126c_1^4 - 495c_1^3/2 + 333c_1^2c_2 - 933c_1^2/4 + 434c_1c_2 - 205c_1c_3 \\ & - 147c_1 - 92c_2^2 + 194c_2 - 200c_3 + 90c_4 - 535/8)\end{aligned}$$

$$Y_{0,3} = 16B_e^5/\omega_e^4(c_1 + 2) + \ldots$$

$$Y_{0,4} = 16B_e^7/\omega_e^6(- 9c_1^2 + 4c_2 - 24c_1 - 22) + \ldots$$

$$Y_{0,5} = 64B_e^9/\omega_e^8(27c_1^3 - 24c_1c_2 + 4c_3 + 90c_1^2 - 32c_2 + 123c_1 + 72)$$

$$\begin{aligned}Y_{1,0} = {} & \omega_e + B_e^2/\omega_e(- 1155c_1^4/256 - 111c_1^3/32 + 459c_1^2c_2/32 - 33c_1^2/64 + 61c_1c_2/8 - 95c_1c_3/8 + 3c_1/8 \\ & - 67c_2^2/16 - c_2/16 - 15c_3/4 + 25c_4/4 - 3/32) + \ldots\end{aligned}$$

$$Y_{1,1} = 6B_e^2c_1/\omega_e + \ldots$$

$$Y_{1,2} = 6B_e^4/\omega_e^3(- 9c_1^2 - 12c_1 + 8c_2 - 4) + \ldots$$

$$Y_{1,3} = 4B_e^6/\omega_e^5(189c_1^3 - 264c_1c_2 + 80c_3 + 396c_1^2 - 256c_2 + 336c_1 + 128) + \ldots$$

$$Y_{2,0} = B_e(- 15c_1^2/8 + 3c_1/2 + 3c_2/2 - 3/4) + \ldots$$

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

$$\begin{aligned}Y_{2,2} = {} & B_e^5/\omega_e^4(- 1080c_1^4 + 2484c_1^2c_2 - 624c_2^2 - 1140c_1c_3 + 360c_4 - 1566c_1^3 + 1992c_1c_2 \\ & - 480c_3 - 981c_1^2 + 264c_2 - 396c_1 - 87/2) + \ldots\end{aligned}$$

$$\begin{aligned}Y_{3,0} = {} & B_e^2/\omega_e(- 705c_1^4/64 + 15c_1^3/8 + 225c_1^2c_2/8 + 57c_1^2/16 - 17c_1c_2/2 - 35c_1c_3/2 \\ & - 2c_1 - 17c_2^2/4 - 3c_2/4 + 5c_3 + 5c_4 + 1/2)\end{aligned}$$

$$\begin{aligned}Y_{3,1} = {} & B_e^4/\omega_e^3(19035c_1^5/32 - 7545c_1^3c_2/4 + 2175c_1^2c_3/2 + 2055c_1c_2^2/2 - 510c_1c_4 - 450c_2c_3 \\ & + 140c_5 + 450c_1^4 - 780c_1^2c_2 + 300c_1c_3 + 345c_1^3/4 + 45c_1c_2 - 20c_3 + 15c_1^2) + \ldots\end{aligned}$$

$$\begin{aligned}Y_{4,0} = {} & B_e^3/\omega_e^2(- 115755c_1^6/1024 + 116325c_1^4c_2/256 - 9765c_1^3c_3/32 - 24945c_1^2c_2^2/64 + 2715c_1^2c_4/16 \\ & + 2415c_1c_2c_3/8 - 315c_1c_5/4 + 375c_2^3/16 - 165c_2c_4/4 - 315c_3^2/8 + 35c_6/2 - 855c_1^5/256 - 1215c_1^3c_2/32 \\ & + 615c_1^2c_3/16 - 165c_1c_4/4 + 1125c_1c_2^2/16 - 165c_2c_3/4 + 35c_5/2 + 18855c_1^4/512 - 5565c_1^2c_2/64 \\ & + 705c_1c_3/16 + 195c_2^2/32 - 45c_4/8 - 45c_1^3/8 + 45c_1c_2/2 - 10c_3 - 135c_1^2/32 - 5c_2/8 + 15c_1/8 - 5/16) + \ldots\end{aligned}$$

Table 2. Expressions for coefficients $Z_{kl}^{r,a}$ for vibrational and rotational nonadiabatic effects

$$Z_{0,1}^{r,a}M_a/m_e = B_et_0^a \qquad Z_{0,2}^{r,a}M_a/m_e = B_e\gamma^2[- s_0^a - 2t_0^a + t_1^a]$$

$$Z_{0,3}^{r,a}M_a/m_e = B_e\gamma^4[s_0^a(3c_1/2 + 9/2) - \tfrac{1}{2}s_1^a + t_0^a(3c_1 + 6) + t_1^a(- 3c_1/2 - 4) + t_2^a]$$

$$\begin{aligned}Z_{0,4}^{r,a}M_a/m_e = {} & B_e\gamma^6[s_0^a(- 9c_1^2/2 + 2c_2 - 33c_1/2 - 39/2) + s_1^a(3c_1/2 + 19/6) - \tfrac{1}{3}s_2^a + t_0^a(- 9c_1^2 \\ & + 4c_2 - 24c_1 - 22) + t_1^a(9c_1^2/2 - 2c_2 + 15c_1 + 65/4) + t_2^a(- 3c_1 - 6) + t_3^a]\end{aligned}$$

$$\begin{aligned}Z_{0,5}^{r,a}M_a/m_e = {} & B_e\gamma^8[s_0^a(135c_1^3/8 - 15c_1c_2 + 5c_3/2 + 585c_1^2/8 - 26c_2 + 993c_1/8 + 699/8) \\ & + s_1^a(- 45c_1^2/8 + 2c_2 - 69c_1/4 - 267/16) + s_2^a(3c_1/2 + 11/4) - \tfrac{1}{4}s_3^a + t_0^a(135c_1^3/4 - 30c_1c_2 \\ & + 5c_3 + 225c_1^2/2 - 40c_2 + 615c/4 + 90) + t_1^a(- 135c_1^3/8 + 15c_1c_2 - 5c_3/2 - 135c_1^2/2 + 24c_2 \\ & - 213c_1/2 - 70) + t_2^a(45c_1^2/4 - 4c_2 + 33c_1 + 61/2) + t_3^a(- 9c_1/2 - 8) + t_4^a]\end{aligned}$$

$$Z^{r,a}_{1,1}M_a/m_e = B_e\gamma[s^a_0(3c_1/2 + 3/2) - \tfrac{1}{2}s^a_1 + 3t^a_0c_1 + t^a_1(- 3c_1/2 - 1) + t^a_2]$$

$$Z^{r,a}_{1,2}M_a/m_e = B_e\gamma^3[s^a_0(- 27c_1^2/4 + 6c_2 - 63c_1/4 - 21/2) + s^a_1(9c_1/4 + 7/2) - s^a_2 + t^a_0(- 27c_1^2/2$$

$$+ 12c_2 - 18c_1 - 6) + t^a_1(27c_1^2/4 - 6c_2 + 27c_1/2 + 27/4) + t^a_2(- 9c_1/2 - 6) + 3t^a_3]$$

$$Z^{r,a}_{1,3}M_a/m_e = B_e\gamma^5[s^a_0(567c_1^3/16 - 99c_1c_2/2 + 15c_3 + 1755c_1^2/16 - 141c_2/2 + 261c_1/2 + 69)$$

$$+ s^a_1(- 189c_1^2/16 + 15c_2/2 - 27c_1 - 171/8) + s^a_2(9c_1/2 + 15/2) - 3s^a_3/2 + t^a_0(567c_1^3/8 - 99c_1c_2 + 30c_3$$

$$+ 297c_1^2/2 - 96c_2 + 126c_1 + 48) + t^a_1(- 567c_1^3/16 + 99c_1c_2/2 - 15c_3 - 783c_1^2/8 + 63c_2 - 819c_1/8$$

$$- 183/4) + t^a_2(189c_1^2/8 - 15c_2 + 99c_1/2 + 69/2) + t^a_3(- 27c_1/2 - 21) + 6t^a_4]$$

$$Z^{r,a}_{2,1}M_a/m_e = B_e\gamma^2[s^a_0(45c_1^3/8 - 39c_1c_2/4 + 15c_3/4 + 9c_1^2 - 9c_2/4 + 117c_1/16 + 3/16)$$

$$+ s^a_1(- 15c_1^2/8 + 3c_2/4 - 29c_1/8 - 13/32) + s^a_2(5c_1/4 + 5/8) - 3s^a_3/8 + t^a_0(45c_1^3/4 - 39c_1c_2/2$$

$$+ 15c_3/2 + 27c_1^2/4 + 3c_1/8) + t^a_1(- 45c_1^3/8 + 39c_1c_2/4 - 15c_3/4 - 57c_1^2/8 + 3c_2/2$$

$$- 27c_1/8 + 3/8) + t^a_2(15c_1^2/4 - 3c_2/2 + 6c_1) + t^a_3(- 15c_1/4 - 3/2) + 3t^a_4/2]$$

Table 3. Expressions for coefficients $Z^{v,a}_{kl}$ for vibrational adiabatic and nonadiabatic effects

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$$Z^{v,a}_{0,0}M_a/m_e = u^a_0 \qquad Z^{v,a}_{0,1}M_a/m_e = \gamma^2u^a_1$$

$$Z^{v,a}_{0,2}M_a/m_e = B_e\gamma^2s^a_0 + \gamma^4[u^a_1(- 3c_1/2 - 2) + u^a_2]$$

$$Z^{v,a}_{0,3}M_a/m_e = B_e\gamma^4[s^a_0(- 3c_1/2 - 9/2) + \tfrac{1}{2}s^a_1] + \gamma^6[u^a_1(9c_1^2/2 - 2c_2 + 9c_1 + 25/4) + u^a_2(- 3c_1 - 4) + u^a_3]$$

$$Z^{v,a}_{0,4}M_a/m_e = B_e\gamma^6[s^a_0(9c_1^2/2 - 2c_2 + 33c_1/2 + 39/2) + s^a_1(- 3c_1/2 - 19/6) + \tfrac{1}{3}s^a_2] + \gamma^8[u^a_1(- 135c_1^3/8 +$$

$$15c_1c_2 - 5c_3/2 - 45c_1^2 + 16c_2 - 99c_1/2 - 47/2) + u^a_2(45c_1^2/4 - 4c_2 + 24c_1 + 33/2) + u^a_3(- 9c_1/2 - 6) + u^a_4]$$

$$Z^{v,a}_{1,0}M_a/m_e = \gamma^{-1}B_es^a_0 + \gamma[u^a_1(-3c_1/2 + 1) + u^a_2]$$

$$Z^{v,a}_{1,1}M_a/m_e = B_e\gamma[- 3s^a_0/2 + 3s^a_1/2] + \gamma^3[u^a_1(27c_1^2/4 - 6c_2 + 9c_1/2 + 3/4) - 9u^a_2c_1/2 + 3u^a_3]$$

$$Z^{v,a}_{1,2}M_a/m_e = B_e\gamma^3[s^a_0(27c_1^2/8 - 3c_2 + 45c_1/4 + 9) + s^a_1(-9c_1 - 22)/4 + 2s^a_2] + \gamma^5[u^a_1(-567c_1^3/16 + 99c_1c_2/2$$

$$- 15c_3 - 405c_1^2/8 + 33c_2 - 243c_1/8 - 39/4) + u^a_2(189c_1^2/4 - 30c_2 + 45c_1 + 9)/2 + u^a_3(-27c_1/2 - 9) + 6u^a_4]$$

$$Z^{v,a}_{2,0}M_a/m_e = B_e[s^a_0(-15c_1^2/4 + 3c_2 + 3c_1 - 3/2)/2 + s^a_1(-3c_1/4 + \tfrac{1}{2}) + \tfrac{1}{2}s^a_2] + \gamma^2[u^a_1(- 45c_1^3/8 + 39c_1c_2/4$$

$$- 15c_3/4 + 3c_1^2/8 - 3c_2/2 + 9c_1/8 - 3/8) + u^a_2(15c_1^2/4 - 3c_2/2 -3c_1/2) + u^a_3(- 15c_1/4 + 3/2) + 3u^a_4/2]$$

$$Z^{v,a}_{2,1}M_a/m_e = B_e\gamma^2[s^a_0(45c_1^3/8 - 39c_1c_2/4 + 15c_3/4 - 9c_1^2/4 + 9c_2/4 - 111c_1/16 - 3/16) + s^a_1(9c_1^2/4$$

$$- 9c_2/4 + 65c_1/8 + 1/32) + s^a_2(- 11c_1/4 - 5/8) + 15s^a_3/8] + \gamma^4[u^a_1(135c_1^4/2 - 621c_1^2c_2/4 + 285c_1c_3/4$$

$$+ 39c_2^2 - 45c_4/2 + 423c_1^3/8 - 66c_1c_2 + 15c_3 + 63c_1^2/4 - 15c_2/8 + 33c_1/8 + 3/32) + u^a_2(- 45c_1^3$$

$$+ 117c_1c_2/2 - 15c_3 - 81c_1^2/4 - 3c_1/4) + u^a_3(135c_1^2/4 - 39c_2/2 + 27c_1/2 + 3/8) - 39u^a_4c_1/2 + 15u^a_5/2]$$

$$Z^{v,a}_{3,0}M_a/m_e = B_e\gamma[s^a_0(- 2115c_1^4/256 + 675c_1^2c_2/32 - 51c_2^2/16 - 105c_1c_3/8 + 15c_4/4 + 45c_1^3/32 + \tfrac{1}{4}c_2$$

$$+ 15c_3/4 + 171c_1^2/64 - 9c_2/16 - 3c_1/2 + 3/8) + s^a_1(- 15c_1^3/32 + 17c_1c_2/8 - 5c_3/4 - 31c_1^2/16 - 51c_1c_2/8$$

$$+ 27c_1/16 - \tfrac{1}{2}) + s^a_2(5c_1^2/16 + \tfrac{1}{4}c_2 + \tfrac{1}{4}c_1 - 3/8) + s^a_3(- 5c_1/4 + \tfrac{1}{2}) + \tfrac{1}{2}s^a_4] + \gamma^3[u^a_1(- 19035c_1^5/512$$

$$+ 7545c_1^3c_2/64 - 2175c_1^2c_3/32 - 2055c_1c_2^2/32 + 255c_1c_4/8 + 225c_2c_3/8 - 35c_5/4 - 855c_1^4/256 - 15c_1^2c_2/32$$

$$+ 25c_1c_3/8 + 85c_2^2/16 - 15c_4/4 + 1005c_1^3/128 - 425c_1c_2/32 + 65c_3/16 - 15c_1^2/32 + 13c_2/8 - 9c_1/16$$

$$+ 1/8) + u^a_2(6345c_1^4/256 - 1575c_1^2c_2/32 + 175c_1c_3/8 + 85c_2^2/16 - 15c_4/4 - 105c_1^3/32 + 85c_1c_2/8$$

$$- 15c_3/4 - 285c_1^2/64 + 9c_2/16 + 3c_1/2 - 1/8) + u^a_3(- 705c_1^3/32 + 225c_1c_2/8 - 35c_3/4 + 45c_1^2/16$$

$$- 17c_2/4 + 57c_1/16 - 1) + u^a_4(225c_1^2/16 - 17c_2/4 - 17c_1/4 - 3/8) + u^a_5(- 35c_1/4 + 5/2) + 5u^a_6/2]$$

of the form $(d/dx)x^j(d/dx)$, we assumed that $\beta(R)$ is a sufficiently well behaved function; we took $\beta(R)$ to be the local representation near $R=R_e$ of a function that possesses the correct asymptotic properties at $R=0$ and $R\rightarrow\infty$, and carried the function $\beta(R)$ through all calculations until the final stage so as to avoid problems with the asymptotic behaviour of the polynomial form $\beta(x)$ or $\beta(z)$. Because the ratios $\kappa^4 \equiv m_e/M_{at}$ and $\gamma^2 \equiv (4B_e^2/\omega_e^2)$ have comparable magnitudes, to include in $Z_{kl}^{r,v}$ further contributions that contain successive factors γ^2 would be inconsistent without including terms proportional to $(m_e/M_{at})^2$; therefore only the leading contributions to $Z_{kl}^{r,v}$ appear in tables 2 and 3. A much larger collection of these expressions of $Z_{kl}^{r,v}$ and their derivatives with respect to the parameters will be published subsequently in machine-readable form.

All these expressions Y_{kl} and $Z_{kl}^{r,v}$ we have produced by methods of symbolic computation,[15] first in the form containing the appropriate coefficients of x^j;[7] we then converted the coefficients a_j, $\eta_j^{a,b}$, $\zeta_j^{a,b}$ and $\Xi_j^{a,b}$ of x^j into the present ones c_j, $u_j^{a,b}$, $t_j^{a,b}$ and $s_j^{a,b}$ of z^j respectively. For these analytic computations, we employed two separate processors Maple and Reduce to verify the accuracy of the independent results; the expressions and their partial derivatives with respect to the parameters were similarly converted into efficiently executable Fortran code for subsequent numerical applications.

3. NUMERICAL TREATMENT

The objective of this work is to enable in one stage the evaluation of parameters of the pertinent radial functions from the frequencies and wavenumbers of the pure rotational and vibration-rotational spectral transitions. As spectral lines of a particular molecular species are in general much more numerous than the parameters of the radial functions that one seeks to represent the frequencies or wavenumbers of the lines in the most compact and physically meaningful form, we require a statistically based process of reduction of the frequencies and wavenumbers of measured transitions. The wavenumbers of pure rotational or vibration-rotational transitions to which have been assigned sets of quantum numbers to specify the initial and final states of a particular isotopic variant are the differences of the spectral terms, $\tilde{\nu} = E_{v'J'} - E_{vJ}$. Because of the nonlinear dependence on the ultimate parameters k_e, R_e, c_j, $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ of these wavenumbers through the intermediate quantities, namely the vibration-rotational terms E_{vJ}, the coefficients Y_{kl} and various Z_{kl}, only indirect or iterative methods of solution are applicable. For this purpose we use an algorithm that Newton originated, to which Gauss and Cauchy contributed subsequently, and in which particular techniques of decomposition of the normal equations and improvements thereto are due to Choleski, Hammarling, Levenberg, Marquadt and Morrison.[16,17] To ensure the least biased and most precise values of resulting parameters,[18] the criterion of best fit is the least sum of the squares of the residuals; the latter are the differences between the observables (the measured wavenumbers or frequencies converted to wavenumbers) and the values of the transition wavenumbers calculated by means of equations 9 and 12. Our calculation employs analytic expressions of the partial derivatives of the residuals with respect to the parameters. The process is therefore a direct fit of wavenumbers of transitions as the dependent variable; the atomic masses and the initial and final, vibrational and rotational quantum numbers are the independent variables within simple but extensive functions, implicit in equation 9. To extend the applicability of the algorithm to transitions involving electronic states other than $^1\Sigma$, there is provision to include further appropriate indices as independent variables. We include the possibility to assign to each datum (the measured wavenumber) an uncertainty reflecting the absolute precision of its measurement; this uncertainty is converted into a weight as the inverse of the squared uncertainty and correlations between measurements are generally neglected. The criterion of convergence of the calculation is that in consecutive iterations the square root of the sum of the squares of the weighted residuals changes less than 0.1 per cent; the actual tolerance in a particular determination depends on both the precision of the data and the consistency of the various sets of data that are included in the collection of wavenumbers to be fitted. The results are the selected parameters in the sets consisting of k_e, R_e and the coefficients c_j, $u_j^{a,b}$, $t_j^{a,b}$ and $s_j^{a,b}$, accompanied by the estimated standard errors (square root of the variance) and the matrix of correlation coefficients (related to the covariances). The auxiliary quantities Y_{kl} and various Z_{kl} are also evaluated directly from the primary parameters if required. Which parameters are included to fit a particular set of data, and initial estimates of these parameters, are subject to initial selection, influenced by both the maximum values of the quantum numbers v and J in the data set and the relative magnitude of γ; the criterion to decide the composition of the ultimate set of parameters is the F-statistic.[19] Generally we either discard a confirmed outlier, any particular datum for which the residual exceeds five estimated standard deviations of its measurement, or accord to it a decreased weight such that its continued presence in further fits has a negligible influence on the subsequently determined parameters. Each such outlier is subjected to examination to ascertain whether any physical explanation, such as alternative assignment, might be deduced, before its presence is attributed to a blunder of measurement.

4. TESTS OF THE ALGORITHM AND APPLICATIONS

In order to demonstrate that this approach to the analysis of the frequencies and wavenumbers of spectral lines is practicable, we have generated test data with assumed values of the parameters in finite sets. First only the parameters $U_{1,0}$, $U_{0,1}$ and c_j, $1 \leqslant j \leqslant 8$, of a single diatomic species specified by one mass of each nucleus were assigned finite values; thus only the quantities Y_{kl} were required. We selected 238 transitions in R and P branches within the range of states $0 \leqslant v \leqslant 7$ and $0 \leqslant J \leqslant 40$. The input wavenumbers were specified to a precision 0.0001 m^{-1} in the range/m^{-1} [2000, 2027000]; the initial values of all parameters were zero except for $U_{1,0}$, $U_{0,1}$ and c_1-c_3 which were given rounded values within about 30 per cent of the set values used to generate the data. During the fit, the sum of the squares of the residuals decreased from 4.56×10^{11} m^{-2} to 1.0×10^{-5} m^{-2}, at which point the standard deviation of the residuals was 2.1×10^{-4} m^{-1} (or double the precision of the input data). The final estimates of the parameters agreed with the set values generally within two (small) standard errors of the former; in the correlation matrix, magnitudes of only four elements of the 45 independent values exceeded 0.95. The results of this test prove that to determine in one stage the potential-energy coefficients from the transition wavenumbers is practicable. In the second test, also of a single isotopic species, the set of assumed parameters of the first test was enhanced to include four coefficients t_j^a, $1 \leqslant j \leqslant 4$; the value of t_0^a was constrained to zero during the fitting process. The same 238 transitions as in the first test but with the correspondingly adjusted wavenumbers were selected. At convergence the standard deviation of the residuals was 2.2×10^{-4} m^{-1}; the generated values of the parameters again agreed with the set values within about two estimated standard errors of the former, but the magnitudes of only two elements of the augmented correlation matrix exceeded 0.95. These results indicate that to determine both the potential-energy coefficients c_j and one set of coefficients reflecting the additional rotational effects is practicable. In the third test, data were analogously simulated for a diatomic molecule like HCl having three supposed isotopic variants, $^1A^{35}B$, $^1A^{37}B$ and $^2A^{35}B$, with 187 transitions of each species within the ranges $0 \leqslant v \leqslant 8$ and $0 \leqslant J \leqslant 41$ in P and R branches. The parameters used to generate the transition wavenumbers numbered 24, comprising $U_{1,0}$, $U_{0,1}$, c_j with $1 \leqslant j \leqslant 8$, u_j^a with $1 \leqslant j \leqslant 4$, u_j^b with $1 \leqslant j \leqslant 2$, t_j^a with $0 \leqslant j \leqslant 4$, and t_j^b with $0 \leqslant j \leqslant 2$. During the fit to the same 24 parameters, the sum of the squares of the residuals decreased from 1.2×10^{12} m^{-2} to 2.1×10^{-4} m^{-2}, at which point the standard deviation of the residuals was 1.9×10^{-4} m^{-1}. As in the previous tests most deduced values of the parameters were within about two standard errors of the set values; although the magnitudes of several elements of the parameter correlation matrix were near unity, especially those connecting $t_0^{a,b}$ with $u_1^{a,b}$, $t_1^{a,b}$ and a few other parameters, the quality of the fit indicated that the programme was capable of proper operation to reproduce the realistically set values of the parameters. Hence the results of this test demonstrate that to evaluate not only the potential-energy coefficients c_j but also simultaneously four sets of other coefficients, namely t_j^a, t_j^b, u_j^a and u_j^b (in the neglect of s_j^a and s_j^b) related to the adiabatic and nonadiabatic effects apportioned to particular atomic centres, is practicable by means of this algorithm and its present implementation.

Following these tests of our programme we undertook the analysis of spectral data from pure rotational and vibration-rotational transitions of isotopic variants of several diatomic species. We present here the results for HCl that not only furnish a practical test of the programme but also are of intrinsic interest. The data set consisted of 1066 lines of the variants $^1H^{35}Cl$ (482 lines), $^1H^{37}Cl$ (314 lines), $^2H^{35}Cl$ (136 lines), $^2H^{37}Cl$ (132 lines) and one pure rotational transition of each of $^3H^{35}Cl$ and $^3H^{37}Cl$. This set included the best or not superseded data from our previous global fit,[20] complemented by the following more recent data: pure rotational lines of $^1H^{35}Cl$ and $^1H^{37}Cl$[21] and of $^2H^{35}Cl$ and $^2H^{37}Cl$,[22] the newly remeasured fundamental vibration-rotational bands of $^1H^{35}Cl$ and $^1H^{37}Cl$[23] and of $^2H^{35}Cl$ and $^2H^{37}Cl$,[24] and the emission lines in the sequence $\Delta v=1$ of $^1H^{35}Cl$ and $^1H^{37}Cl$.[25] During the fit the values of t_0^H and t_0^{Cl} were constrained to those consistent with the known value[26] of the rotational magnetogyric ratio g_J according to the partition formulae,[27] and all other parameters were constrained to null values. The results are presented in table 4, in which the range of validity of the radial functions is also specified. All 19 independent parameters had significant values; for only six of 171 independent correlation coefficients of the parameters the magnitudes exceeded 0.95, the largest being 0.983, but there were no systematic features or trends in these values.

5. DISCUSSION

Examination of the expressions in tables 2 and 3 leads one to conclude that the parameters within a particular set of functions $Z_{kl}^{r,a}$ and $Z_{kl}^{v,a}$ (and correspondingly for the nucleus of other atomic number) number more than one can determine from available data. For instance, application of equation 11 to fit the same set of 1066 data yielded the significant determination of $U_{k,0}$ with $1 \leqslant k \leqslant 5$, $U_{k,1}$ with $0 \leqslant k \leqslant 4$, $\Delta_{1,0}^H$, $\Delta_{2,0}^H$, $\Delta_{0,1}^H$, $\Delta_{1,1}^H$, $\Delta_{0,2}^H$, $\Delta_{0,3}^H$, $\Delta_{1,0}^{Cl}$ and $\Delta_{0,1}^{Cl}$. The values of these U_{kl} and the derived coefficients c_j are similar to those of $U_{1,0}$, $U_{0,1}$ and c_j with $1 \leqslant j \leqslant 8$ given in table 4. The values of the parameters Δ_{kl}^H and Δ_{kl}^{Cl} are proportional to the sums $Z_{kl}^H = Z_{kl}^{r,H} + Z_{kl}^{v,H}$ and $Z_{kl}^{Cl} = Z_{kl}^{r,Cl} + Z_{kl}^{v,Cl}$, respectively, that result from combination of the expressions in tables 2 and 3 or from those containing the corresponding coefficients of x^j.[7] In either case only six values of the coefficients Δ_{kl}^H are available to determine ten parameters comprising u_j^H with $1 \leqslant j \leqslant 4$, t_j^H with $0 \leqslant j \leqslant 2$ and s_j^H with $0 \leqslant j \leqslant 2$; seven values of Z_{kl}^H are effectively available because we provided the value of t_0^H (and t_0^{Cl}) from supplementary experimental measurements. In these circumstances we constrain to zero all parameters s_j^H in order to derive the values of t_j^H and u_j^H presented in table 4. Hence only u_1^H (and analogously u_1^{Cl}) represents purely the vibrational adiabatic effects (as the expression for $Z_{0,1}^{v,a}$ in table 3 makes clear), whereas the remaining values of u_j^H and t_j^H absorb to an unknown extent the values of the indeterminate parameters s_j^H with $0 \leqslant j \leqslant 2$ describing the vibrational nonadiabatic effects. In order to determine the latter parameters, one requires knowledge of the rotational and vibrational dependence of the rotational magnetogyric ratio g_J; the rotational dependence would lead to t_1^H (and t_1^{Cl}) and the vibrational dependence in addition would provide a value of t_2^H (and t_2^{Cl}). Such experimental measurements of the rotational dependence of g_J (which is actually the expectation value $\langle vJ|g(R)|vJ \rangle$) are rare, and only a few instances are known of molecular species for which even the vibrational dependence of g_J has been determined. If these data were known for HCl (any particular isotopic variant), then to determine s_j with $0 \leqslant j \leqslant 2$ would still require a value of $\Delta_{0,4}^H$ according to the use of equation 11; the latter value cannot be determined significantly from the present set of spectral transitions, but measurements of wavenumbers with increased precision might yield this value.

Can the term coefficients Z_{kl}^r be evaluated independently of Z_{kl}^v? The results of the second test with simulated spectral data appear to indicate a partially affirmative answer. To enable a definitive decision, we applied the fitting programme to only the 482 spectral transitions of $^1H^{35}Cl$, for which isotopic variant the available data are most abundant. The set of fitting parameters included only the potential-energy coefficients c_j, $1 \leqslant j \leqslant 8$, $U_{0,1}$, $U_{1,0}$, t_1 and t_2 with t_0^H and t_0^{Cl} constrained and all others zero. Under these conditions in relation to equation 7, the proper mass coefficient of the composite quantities t_1 and t_2 is the reduced molecular mass μ, not M_H; we have accordingly adjusted the results of t_1^H and t_2^H produced by our programme. The values of $U_{0,1}$, $U_{1,0}$ and c_j with $1 \leqslant j \leqslant 8$ derived from this fit are similar to those in table 4, differing in each instance by several standard errors, as expected because in this determination the potential-energy coefficients absorb the vibrational adiabatic and (to some extent) nonadiabatic effects. The remarkable results are that $t_1=-0.5582 \pm 0.0090$ and $t_2= -1.844 \pm 0.093$, to be compared with the values $t_1^H=-0.5415 \pm 0.0127$ and $t_2^H=-1.752 \pm 0.068$ in table 4. Although this excellent agreement proves conclusively that one can experimentally separate the vibrational Z_{kl}^v and extra rotational Z_{kL}^r contributions to the vibration-rotational energies, even if the contributions of the individual atomic nuclei cannot be derived from data of only one isotopic variant, this discovery fails to assist the evaluation of the parameters $s_j^{H,Cl}$ related to the vibrational nonadiabatic effects.

Table 4. Coefficients of Radial Functions and Other Molecular Properties of HCl X $^1\Sigma^+$, all Independent of Mass.[a]

j	c_j	t_j^{Cl}	t_j^{H}	$u_j^{Cl}/10^6 m^{-1}$	$u_j^{H}/10^6 m^{-1}$
0	$(21114065.63 \pm 1.84)\ m^{-1}$	0.09966^*	0.45673^*		
1	-1.3634913 ± 0.0000093	-1.056 ± 0.248	-0.5415 ± 0.0127	-4.217 ± 0.27	-6.1254 ± 0.0033
2	0.865701 ± 0.000045		-1.752 ± 0.068	21.033 ± 0.85	18.4541 ± 0.0125
3	-0.468877 ± 0.00060				-13.430 ± 0.53
4	0.07426 ± 0.0033				8.70 ± 2.4
5	0.14714 ± 0.0079				
6	-0.5422 ± 0.054		$U_{1,0} = (296032.211 \pm 0.043)\ m^{-1}\ u^{1/2}$		
7	-1.1354 ± 0.192		$U_{0,1} = (1037.63850 \pm 0.00021)\ m^{-1}\ u$		
8	9.829 ± 0.41		$k_e = (516.33132 \pm 0.00034)\ N\ m^{-1}$		
	range $0.98 \leqslant R/10^{-10}\ m \leqslant 1.92$		$R_e = (1.27460388 \pm 0.00000108) \times 10^{-10}\ m$		

[a]Each stated uncertainty represents one estimated standard error; the F-value of the fit of 1066 data with 19 unconstrained and two constrained* parameters (apart from those set to zero value) is 1.82×10^{16}, and the normalised standard deviation $\hat{\sigma}$ is 1.284.

Comparison of the values in table 4 with published results is appropriate. The agreement with our previous results[20] or their equivalent is reasonable when one takes into account the greatly increased precision of the pure rotational transitions and fundamental vibration-rotational lines used in the present work, which also employs more accurate values of the atomic masses and fundamental physical constants.[28,29] Comparison with the results of Coxon and Hajigeorgiou[30] is more difficult because, although they included no recent rotational and vibration-rotational data, their electronic spectra enabled much more extensive (although only moderately precise) data up to $v=17$ for $^1H^{35}Cl$ and $v=24$ for $^2H^{35}Cl$; for $V^{BO}(R)$ they employed exponential functions instead of our representation $V^{BO}(z)$. Coxon's comparison of z and exponential representations for the same data set of LiH demonstrated that the former was both more economical, 17 vs 19 unconstrained parameters, and more reliable, in that even with the extra parameters in the exponential case some were poorly defined;[31] furthermore the fitting process appears unreliable because h_3^{Li} rather than c_6 of LiH was evaluated[31] whereas the reverse case provides a more realistic description of the data.[32] Thus our representations in terms of the variable z are demonstrated to be superior to those in terms of the exponential functions,[31] apart from the fact that these exponential functions possess quantitatively incorrect asymptotic behaviour in the approach to the dissociation limit. The radial functions[30,31] other than that for potential energy derived for both HCl and LiH have no particular physical significance, whereas in the present work we demonstrate that the use of the values of t_0^H and t_0^{Cl} derived from the magnetogyric ratio g_J permits at least the values of $u_1^{H,Cl}$ to be associated specifically with vibrational adiabatic effects. In a further analysis (with E. Tiemann) of spectra of LiH according to two distinct numeric approaches based on analytic expressions for Y_{kl}, we have derived significant values of $s_0^{H,Li}$; for LiH this achievement was practicable because of both the strongly electrically dipolar nature of this molecular species and the set of spectral data more coherent than those available for HCl analysed here. These two values[30] of R_e, that differ by 43 standard errors of the more precisely specified value, suffer from systematic error because no account was taken of the nonzero value of g_J or $t_0^{H,Cl}$; the standard errors[30] fail to take into account the uncertainties of the fundamental constants.

The use of the analytic expressions in tables 1-3 enables one for the first time to distinguish purely from experimental data the effects attributed to adiabatic, nonadiabatic rotational and vibrational effects. These effects are not truly physical in nature because they arise from the approximations inherent in the separate treatment of electronic and nuclear motions; however the radial functions for the nonadiabatic rotational effects in particular are directly related, within the Born-Oppenheimer approximation to the molecular rotational magnetogyric ratio which is a physically observable quantity. The knowledge of the operation of all these effects is important so that one can ensure the correct treatment of the effects of nuclear mass in the process of spectral reduction, even according to an essentially empirical relation such as equation 11. Although these expressions were produced by means of a wave-mechanical approach, i.e. through the use of the Schrodinger equation, they are independent of that particular method of generation; we could equally well have produced them in identical form by means of perturbation theory in matrix mechanics or Dirac's method of operators. The use of these expressions is simpler, more reliable and computationally more efficient than fully numerical approaches, such as the repeated solution of the Schrodinger equation by finite differences, because mainly substitutions into these expressions and their analytic derivatives with respect to the parameters are involved in the fitting process.

6. CONCLUSIONS

We have demonstrated to be practicable the evaluation of separate radial functions for the potential energy, vibrational adiabatic, and vibrational and rotational nonadiabatic effects from experimental spectral data, provided that supplementary data of the rotational and vibrational dependence of the rotational magnetogyric ratio are included in the analysis. To estimate a value of the rotational g factor by fitting of the only vibration-rotational transitions in the absence of applied fields is difficult but in the case of AlH this attempt was successful; the relatively large value so deduced indicates that the electronic ground state may be either paramagnetic or much less diamagnetic than expected for a state of type $^1\Sigma^+$. Moreover with the available spectral information on ArH^+ X $^1\Sigma^+$ our method may be applied to even this molecular ion and to similar species. Because the variation of the isotopic mass and the extra rotational dependence of the frequencies of vibration-rotational transitions provide for nuclei of each distinct atomic number information of only two kinds beyond the potential energy which is the dominant effect, whereas further effects of three kinds--adiabatic and nonadiabatic vibrational and rotational--remain to be determined, these supplementary data from the vibrational and rotational dependence of the rotational magnetogyric ratio are required in the analysis. As such data are extremely sparse, measurements of the Zeeman effect on lines in radio-frequency transitions or in pure rotational and fundamental vibration-rotational bands of appropriate molecular species are warranted. The large dopplerian widths of vibration-rotational lines (for instance, $\sim 0.6\ m^{-1}$ for the full width at half the maximum absorbance of lines in the fundamental vibration-rotational band of $^1H^{35}Cl$ at 300 K) demand correspondingly large magnetic flux densities ($B_0 \sim 51$ T for this band of HCl) to effect a splitting of the same magnitude as this dopplerian width, unless one either employs a molecular beam or devises another method to circumvent this width. Measurements of the Zeeman effect in radio-frequency or microwave spectra of molecules in excited rotational and vibrational states may thus enable one to derive these dependences more readily than from vibration-rotational spectra. In the spirit of Dunham's original work,[2] the analytic expressions presented in tables 1-3 enable one to distinguish the pertinent phenomena from pure rotational and vibration-rotational transitions consisting of sufficiently numerous lines of multiple isotopic variants, in combination with the essential supplementary data. By this means fundamental properties that are independent of nuclear mass, so to depend primarily on atomic number, are accurately determined for diatomic molecular species.

Even though in his scientific work Mendeleyev was mainly concerned with topics other than the periodic properties of the chemical elements, the spirit of his enduring accomplishment in the latter direction continues to influence the analysis of molecular spectra, despite the fact that spectroscopy had barely evolved during the latter years of his long life. During Dunham's brief life, molecular spectroscopy had already assumed something like its present form but his contributions endure because of the elegance of his methods and the great physical insight both that guided the development of his methods, as we can read in his papers, and that we can acquire from the application of his methods of analysis to contemporary spectra of the highest precision and resolution. van Vleck's work[4] on adiabatic and nonadiabatic effects was very much in the spirit of Mendeleyev's and Dunham's achievements; possibly if van Vleck had had access to symbolic computation such as that provided by modern processors like Maple, he might have produced results equivalent to those in tables 2 and 3 several decades ago. According to the actual circumstances, we have been able to complete their work so as to enable a comprehensive analysis of the data of observed frequencies and wavenumbers of lines in regular vibration-rotational spectra of diatomic molecules from states not too near the dissociation limit within the precision of these measurements. The treatment of the corresponding spectral data of polyatomic molecules is in progress.[33,34]

7. ACKNOWLEDGMENTS

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