

Algebraic vs. numerical methods for analysing diatomic spectral data: a resolution of discrepancies

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Received 1 December 2003; in revised form 11 March 2004

Available online 20 August 2004

Abstract

The past decade has seen persistent disagreements in the literature and at meetings concerning the validity and physical significance of two different approaches for the reduction of a set of diatomic molecule data to a compact set of parameters defining a potential energy curve and Born–Oppenheimer breakdown (BOB) radial functions. This paper explains the apparent discrepancies between an algebraic method championed by J.F. Ogilvie and a numerical method pioneered by J.A. Coxon. It confirms the validity of the central underlying assumption of both approaches, namely, that spectroscopic data for one or multiple isotopomers can be reduced accurately to a compact set of parameters characterizing the potential energy and BOB radial functions, and it shows that the values of those parameters should not depend on which method is used to determine them. The previously reported discrepancies arose because of a truncation convention applied in Ogilvie’s algebraic RADIATOM code. Because of that convention, eigenvalues of the Schrödinger equation generated using published potential energy and BOB functions determined using RADIATOM will not accurately reproduce the input data used in the analyses. However, if that truncation convention is not applied and the Dunham-type expansions are summed to convergence, algebraic analyses yield results essentially identical to those obtained from direct numerical-fit methods. Tests reported herein also support Watson’s [J. Mol. Spectrosc. 217 (2003) 157] assertion that electric dipole moments and rotational *g*-factors cannot be determined only from transition energy data obtained in the absence of external fields. © 2004 Elsevier Inc. All rights reserved.

1. Introduction

The most common method of reducing diatomic molecule spectral data has traditionally involved representing the dependence of the level energies $E_{v,J}$ on the vibrational and rotational quantum numbers v and J using a type of double power series expression commonly associated with the name of J.L. Dunham, which for a molecule in a $^1\Sigma$ state has the form:

$$E_{v,J} = \sum_m \sum_l Y_{l,m} (v + \frac{1}{2})^l [J(J+1)]^m. \quad (1)$$

Dunham’s theory yielded expressions for the $Y_{l,m}$ coefficients in terms of the coefficients of a power series

expansion representation for the potential energy function, and showed that since those potential function parameters could be determined uniquely from the expansion coefficients for $m = 0$ and 1, the coefficients with $m > 1$ were not independent variables [1–3]. However, in most applications in the literature, all of the expansion coefficients in Eq. (1) are treated as independent parameters. This yields more compact expressions than would be required by a ‘proper’ Dunham analysis (one taking account of the relationship among the $Y_{l,m}$ ’s), but the physical significance of the resulting parameters becomes somewhat reduced.

Over the past decade or so it has become increasingly common to replace empirical fits to energy level expressions such as Eq. (1) by “direct potential fits” in which observed transition energies are compared with eigenvalue differences calculated from the Schrödinger equa-

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Table 1
Dimensionless root mean square deviation \overline{dd} for fits to/predictions of high resolution MW and IR data

Molecule	No. of data	RADIATOM fit			Numerical fit		
		Result	Reference	Numerical test	Result	Reference	RADIATOM test
NaCl	1210	0.904	[32]	16.18	0.918	[36]	4.915
GeS	727	0.948	[30]	4.80	0.927	[37]	4.207
BrCl	883	0.940	[29]	9.35	0.939	[37]	19.029
LiH	594	1.103	[31]	45.0	1.085	[35]	182.6
GaH	1094	0.909	[27]	283.3	0.869	[37]	608.3

tion for some parameterized potential energy function, and a least-squares procedure used to determine optimal values of those parameters. This approach typically reduces a large set of data for single or multiple isotopomers of a given species to a much smaller numbers of empirical parameters than does the conventional approach of fitting to empirical Dunham-type expansions such as Eq. (1). Moreover, the resulting potential functions can provide a realistic way of extrapolating to predict spectral data outside the range of those used in the analysis, and can also be used to predict collisional and other non-spectroscopic properties of the molecular system. However, over the past dozen years some uncertainty regarding the validity of this direct-potential-fit procedure has been raised by a persistent dispute about the validity and physical significance of the results yielded by two different approaches to the problem. One of these is a numerical approach, initially developed for treating triatomic Van der Waals molecules [4], which has been extensively applied to diatomic molecules by a number of research groups [5–21]. The other is the algebraic approach applied in Ogilvie’s RADIATOM code [22–32]. An alternate algebraic method developed by Molski [33,34] has been found to be consistent with the numerical method [35–37], but the reason for the disagreements between the results yielded by Ogilvie’s RADIATOM code and those obtained using other methods has never been understood.

The controversy centers on the fact that when exactly the same potential function model is applied to exactly the same data set, the numerical and RADIATOM methods usually yield somewhat different parameter values, and when the parameter sets determined by one method are used as input to the other, the resulting predictions differ from the experimental data by far more than either the experimental uncertainties or the ‘dimensionless root mean square deviation’ (herein denoted \overline{dd}) associated with the original fit [24,35–40].¹ Table 1 summarizes results of several disagreements of this sort; in these comparisons, results associated with the algebraic method

were obtained using Ogilvie’s program RADIATOM while the numerical-fit results are those of Coxon and co-workers. Results obtained independently using Molski’s ‘DS-cP’ algebraic method agree with the numerical-method results [35–37], so they are not listed separately. The present paper will show that a simple extension of the algebraic approach implemented in RADIATOM can in fact yield the same potential energy and Born–Oppenheimer breakdown (BOB) function parameters as do the numerical and algebraic DS-cP methods, and provide an equivalent fit to the associated data sets.

The following presentation begins with a description of the numerical and algebraic methods and the forms of the potential energy and other radial functions used in this work. The source of the discrepancies is then identified, and numerical tests which confirm that explanation are presented. The question of whether or not electric dipole moments and rotational g -factors can be determined uniquely from analyses of transition energy data alone is then examined.

2. Methods for ‘‘direct-potential-fit’’ diatomic data analysis

2.1. The starting point

The common starting point for all of these treatments is an effective radial Schrödinger equation for the vibration–rotation levels of the electronic state of interest, which includes Born–Oppenheimer breakdown terms which take account both of non-adiabatic coupling to other electronic states and of the adiabatic atomic-mass dependent contribution to the potential energy function. For a neutral diatomic molecule A – B in a $^1\Sigma$ electronic state, it may be written as [8,41–45]

$$-\frac{\hbar^2}{2\mu} [1 + \beta(r)] \frac{d^2 \psi_{v,J}(r)}{dr^2} + [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] \psi_{v,J}(r) + \frac{\hbar^2}{2\mu r^2} [1 + \alpha(r)] [J(J+1)] \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (2)$$

in which μ is the normal reduced mass of the two atoms forming the molecule, $V_{\text{CN}}(r)$ is the ‘‘clamped nuclei’’ electronic potential energy function, $\beta(r)$ and $\alpha(r)$ repre-

¹ A \overline{dd} value of (say) 4.8 means that on average the predictions of the model disagree with experiment by 4.8 times the experimental uncertainty.

sent the effect of the non-adiabatic coupling, and $\Delta V_{\text{ad}}(r)$ is the adiabatic contribution to the potential. Using Watson's notation [43,45], $\beta(r)$, $\alpha(r)$, and $\Delta V_{\text{ad}}(r)$ are all written as sums of radial strength functions for each atom, weighted by the factors m_e/M_A and m_e/M_B , respectively, where m_e is the electron mass and M_A and M_B are the two atomic masses:

$$\beta(r) = (m_e/M_A)Q^A(r) + (m_e/M_B)Q^B(r), \quad (3)$$

$$\alpha(r) = (m_e/M_A)R^A(r) + (m_e/M_B)R^B(r), \quad (4)$$

$$\Delta V_{\text{ad}}(r) = (m_e/M_A)S^A(r) + (m_e/M_B)S^B(r). \quad (5)$$

Dividing Eq. (2) by the factor $[1 + \beta(r)]$, expanding it, and utilizing the fact that $|\beta(r)| \ll 1$ yields the version of the above Hamiltonian usually used for practical work [41,44]:²

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \frac{d^2 \psi_{v,J}(r)}{dr^2} + [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] \psi_{v,J}(r) \\ & + \beta(r)[E_{v,J} - V_{\text{CN}}(r)] \psi_{v,J}(r) + \frac{\hbar^2}{2\mu r^2} [1 + \alpha(r) - \beta(r)] \\ & \times [J(J+1)] \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r). \end{aligned} \quad (6)$$

An alternate version of the above Hamiltonian in which the $\beta(r)[E_{v,J} - V_{\text{CN}}(r)]$ term does not appear and the BOB radial functions have different formal definitions has been derived by Watson [43,45], and the present discussion applies equally to either formulation. The objective of any direct potential fit method is then to determine the optimum effective potential energy function (with or without the term $\beta(r)[E_{v,J} - V_{\text{CN}}(r)]$)

$$\begin{aligned} V_{\text{eff}}(r) = & V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r) + \beta(r)[E_{v,J} - V_{\text{CN}}(r)] \\ & + \frac{\hbar^2}{2\mu r^2} [1 + \alpha(r) - \beta(r)][J(J+1)] \end{aligned} \quad (7)$$

whose eigenvalue differences agree with the observed spectroscopic transition energies within (on average) the experimental uncertainties.

If one wishes to generate realistic predictions of spectral data and other properties outside the range of the observables used in the analysis, the four radial functions appearing in Eq. (7) must be constrained to extrapolate realistically at large and small distances [47–49]. On the other hand, for the more limited objective of data reduction, virtually any analytic forms may be used, as long as the resulting functions are well behaved across the radial interval to which the data are sensitive. Our concern here is only the latter requirement, since it is difficult (though not impossible [50]) to impose the

former on the power series potential form which is central to the algebraic method. As a result, we henceforth consider only radial functions which are power series in the expansion variable³

$$\xi = 2(r - r_e)/(r + r_e) \quad (8)$$

in which r_e is the equilibrium internuclear distance. According to the notation of [26], the radial functions appearing in Eqs. (2)–(6) are then expanded as

$$V_{\text{CN}}(r) = c_0 \xi^2 \left(1 + \sum_{j=1} c_j \xi^j \right), \quad (9)$$

$$\Delta V_{\text{ad}}(r) = (m_e/M_A) \sum_{j=1} u_j^A \xi^j + (m_e/M_B) \sum_{j=1} u_j^B \xi^j, \quad (10)$$

$$\beta(r) = (m_e/M_A) \sum_{j=0} s_j^A \xi^j + (m_e/M_B) \sum_{j=0} s_j^B \xi^j, \quad (11)$$

$$\alpha(r) = (m_e/M_A) \sum_{j=0} t_j^A \xi^j + (m_e/M_B) \sum_{j=0} t_j^B \xi^j. \quad (12)$$

2.2. The numerical approach

The numerical approach applies standard methods [35,51–54] to solve Eq. (6) numerically for all vibration–rotation levels joined by transitions included in the data set. If $\beta(r) \neq 0$ the presence of the third term on the left-hand side of Eq. (6) means that the basic Cooley algorithm [51] must be applied in an iterative self-consistent manner, but that too is straightforward. The partial derivatives of transition energies with respect to the potential parameters $\{p_j\}$ required by the least-squares procedure may readily be generated from the upper and lower state eigenfunctions $\psi_{v,J}(r)$ using the Hellmann–Feynman theorem

$$\frac{\partial E_{v,J}}{\partial p_j} = \left\langle \psi_{v,J}(r) \left| \frac{\partial V_{\text{eff}}(r)}{\partial p_j} \right| \psi_{v,J}(r) \right\rangle. \quad (13)$$

The parameters defining $V_{\text{eff}}(r)$ are then optimized iteratively in a standard non-linear least-squares procedure.

Although the present work focuses on the polynomial-type functions of Eqs. (9)–(12), the numerical approach has most often been applied using potential functions with more sophisticated analytic forms. Indeed, one virtue of this method is that it requires no particular assumptions either about the analytical form of the effective potential energy function or about the patterns of level energy spacings. It simply examines how well differences between eigenvalues of the potential defined by the given set of parameters reproduce the observed transition energies, and adjusts the potential

² A formally equivalent alternate form of this equation which treats the atomic-mass-dependent terms as corrections to the effective radial Hamiltonian for a chosen reference isotopomer has many advantages [46]. However, to facilitate the comparisons of interest here, the Herman–Ogilvie [41,44] formulation is used herein.

³ Other forms of the expansion variable, such as $\xi_{\text{Dun}} = (r - r_e)/r_e$ or $\xi_{\text{SPF}} = (r - r_e)/r$, might also be used, but since Eq. (8) was used in most practical applications of the algebraic method, it is adopted here.

function parameters accordingly. Numerical eigenvalue calculations of this type can be made virtually arbitrarily accurate, are very well understood, have been tested extensively against basis set and other methods, and are in practical use in hundreds of laboratories around the world. Thus, the results of such numerical simulations may reasonably be taken as a reliable test of the degree to which differences between the eigenvalues of any particular potential energy function agree with observed spectroscopic transition energies.

2.3. The conventional algebraic approach

The algebraic method for the analysis of diatomic spectral data is based on the theory for the level energies of a rotating vibrator which was initially developed by Dunham [1,2], and subsequently extended to higher orders by numerous other contributors [22,23,26,55–61]. This approach requires the potential energy and other radial functions appearing in Eq. (7) to be expanded about the potential minimum as power series such as Eqs. (9)–(12).³ Using either semiclassical methods [1] or quantum mechanical perturbation theory [62–65], Eq. (6) is then solved algebraically to yield the closed-form expression for the level energies

$$E_{v,J} = \sum_{l=0} \sum_{m=0} \left(Y_{l,m} + Z_{l,m}^A + Z_{l,m}^B \right) \left(v + \frac{1}{2} \right)^l [J(J+1)]^m. \quad (14)$$

Here, $Y_{l,m} = Y_{l,m}(r_e, \mu, \{c_j\})$ are the usual semiclassical Dunham coefficients, which are known functions of r_e , μ and the potential expansion coefficients $\{c_j\}$ of Eq. (9), and the coefficients $Z_{l,m}^{A,B} = Z_{l,m}^{A,B}(r_e, \mu, \{c_j\}, \{s_j^{A,B}\}, \{t_j^{A,B}\}, \{u_j^{A,B}\})$ are small terms which also depend on the expansion coefficients for the adiabatic and non-adiabatic radial strength functions. With the energy eigenvalues involved in the observed transitions represented by Eq. (14), the various radial-function parameters $\{p_j\} = \{\{c_j\}, \{u_j^A\}, \{u_j^B\}, \{s_j^A\}, \{s_j^B\}, \{t_j^A\}, \{t_j^B\}\}$ which define the associated $Y_{l,m}$, $Z_{l,m}^A$, and $Z_{l,m}^B$ eigenvalue expansion coefficients are then optimized by a non-linear least-squares

fit procedure. Since the “Dunham algebra” on which this approach is based is exact, in principle this method can achieve any desired degree of accuracy for a given potential function of finite order.

The first modern applications of this approach to practical data analysis were by Niay et al. [66] in 1977 and by Maki and Lovas in the early 1980’s [67,68]. However, widespread use of this method was hampered by the limited range of the available algebraic expressions. Beyond the leading $\{l,m\}$ terms these expressions become quite complicated [2], and in the early work they had to be derived by hand. In the early 1980’s Ogilvie showed that use of symbolic computation programs in principle could solve this problem, since they could generate expressions at any chosen level of complexity [22,23,26,59,65]. Since modern versions of such programs (such as Maple) can automatically generate reliable Fortran code, opportunities for human error are minimized.

One point which must be addressed with this method is what range of values should be used for the summations over l and m in Eq. (14). The systematic approach adopted by Ogilvie and implemented in all published work using his program RADIATOM is based on the fact that within the Dunham algebra, a given eigenvalue expansion coefficient $Y_{l,m}$ depends only on potential expansion coefficients c_j for which $j \leq 2l + m - 2$, independent of whether or not any higher-order potential parameters exist. Thus, in an analysis which represents the potential by fitted coefficients $c_0 - c_n$, he chose to truncate those sums and include in Eq. (14) only those $Y_{l,m}$ coefficients with $2l + m - 2 \leq n$, with analogous constraints being used to restrict the number of $Z_{l,m}^A$ and $Z_{l,m}^B$ coefficients to be included. For example, if the potential function was defined in terms of only two expansion coefficients c_0 and c_1 , this means that the Dunham coefficients $Y_{1,0}$, $Y_{0,1}$, $Y_{1,1}$, $Y_{0,2}$, and $Y_{0,3}$ would be the only ones allowed in Eq. (14) (see Fig. 1). This “Ogilvie truncation convention” has been used in all RADIATOM applications of the algebraic method reported to date, and is the source of the discrepancies

	$m=0$	1	2	3	4	5	6	7	8	9	10	11	12
$l=0$			c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}
1	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}		
2	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}				
3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}						
4	c_6	c_7	c_8	c_9	c_{10}								
5	c_8	c_9	c_{10}										
6	c_{10}												

Fig. 1. Highest-order potential parameter c_j contributing to the Dunham coefficient $Y_{l,m}$ for various combinations of l and m .

between the results of numerical-fit and published RADIATOM algebraic-fit analyses.

2.4. The “DS-cP” algebraic approach of Molski

In the conventional algebraic method outlined above, it is necessary to generate $Y_{l,m}$ and $Z_{l,m}^{A,B}$ coefficients for a wide range of values of m . To circumvent this problem, Molski developed an alternate approach which begins by determining precisely the position $r_{v,J}$ of the minimum of the centrifugally distorted effective potential $V_{\text{eff}}(r)$ of Eq. (7) for every (v,J) level. Using symbolic computation methods, $V_{\text{eff}}(r) = V_{\text{eff}}^{\{v,J\}}(r)$ is then re-expanded as a power series in the variable $\eta = (r - r_{v,J})/r_{v,J}$ whose coefficients are known functions of the original parameter set $\{p_j\}$. Applying high-order semiclassical theory [1,2] then yields the level energy expression

$$E(v,J) = b_{v,J} + \sum_{l=0} Y_{l,0}^{\{v,J\}}(v + \frac{1}{2})^l \quad (15)$$

in which $b_{v,J}$ and the Dunham-type coefficients $Y_{l,0}^{\{v,J\}}$ are again explicitly known functions of the original parameter set $\{p_j\}$.⁴ The fact that a separate $V_{\text{eff}}(\eta)$ radial expansion is used for each (v,J) level of each isotopomer means that there is no need for analogs of the $m > 0$ expansion coefficients of Eq. (14), and since the effects of the adiabatic and non-adiabatic radial functions are included in these $Y_{l,0}^{\{v,J\}}(\{p_j\})$ coefficients, there is no need for analogs of the $Z_{l,m}^A$ and $Z_{l,m}^B$ expansion coefficients of Eq. (14). The use of symbolic computation again ensures the accuracy of the resulting expressions and computer program, and in principle this method also should be able to yield arbitrary level of accuracy.

Since Molski’s method merges all of the radial functions of Eqs. (9)–(12) into the single effective potential $V_{\text{eff}}^{\{v,J\}}(r)$, the resulting Dunham-type vibrational expansion coefficients $Y_{l,0}^{\{v,J\}}(\{p_j\})$ depend on the expansion parameters $\{p_j\}$ in a more complex manner than was the case for the conventional algebraic method, so a truncation rule for the summation in Eq. (15) would be more difficult to devise. In his more recent applications, Molski simply extends the algebra until there is no further changes in the fitted parameters and dimensionless root mean square deviation (see, e.g., the discussion of the DS-cP treatment of GaH in [37]).

3. Source of the discrepancies

The implications of the “Ogilvie truncation convention” for the treatment of potential function parameters, described at the end of Section 2.2, are summarized in

⁴ Note that the v -dependence of $r_{v,J}$, and hence also of these $Y_{l,0}^{\{v,J\}}$ coefficients, disappears if there is no $\beta(r)[E_{v,J} - V_{\text{CN}}(r)]$ term in Eqs. (6) and (7).

Fig. 1, which lists the highest-order potential parameter c_j which contributes to each $Y_{l,m}$ coefficient, for a range of values of l and m . According to that convention, if the potential energy function $V_{\text{CN}}(r)$ is defined (for example) purely by non-zero parameters $c_0 - c_4$, the computer algebra in RADIATOM would only include contributions to the level energy expression of Eq. (14) involving the 15 $Y_{l,m}$ coefficients (including $Y_{0,1} = Y_{0,1}(r_e, \mu)$) corresponding to $\{l,m\}$ pairs lying above the dashed line cutting across Fig. 1; similarly, if the potential was defined by the non-zero parameters $c_0 - c_8$, only the 35 coefficients corresponding to $\{l,m\}$ combinations lying above the dotted line would be used.

In support of this convention one could argue that if the potential function is defined only by (say) $c_0 - c_n$, then c_{n+1} , c_{n+2} , and all higher-order potential parameters are not known or cannot be determined, so it might seem inappropriate to include any $Y_{l,m}$ coefficients which depend even partially on them. On the other hand, within Dunham algebra the potential coefficients $c_0 - c_n$ also contribute to *all* $Y_{l,m}$ coefficients with $2l + m - 2 > n$. For example, if $n = 4$ the traditional RADIATOM cutoff criterion would neglect all contributions to $E_{v,J}$ due to $Y_{l,m}$ coefficients for $\{l,m\}$ pairs lying below the dashed line in Fig. 1. However, many of those omitted terms depend mainly on the leading potential function coefficients $c_0 - c_n$, and make non-negligible contributions to eigenvalues calculated using Eq. (14). For example, some 27 of the 30 terms comprising the leading contribution to $Y_{4,0}$ (which lies just below the dashed line in Fig. 1) depend only on $c_0 - c_4$ [3]. Thus, it seems hard to accept that such contributions should simply be ignored.

All published RADIATOM analyses utilized the Ogilvie truncation convention which explicitly omits from Eq. (14) all $Y_{l,m}$ coefficients corresponding to $2l + m - 2 > n$, where c_n is the highest-order non-zero potential coefficient considered in the analysis. Thus, while the fits can be made to ensure that differences between the eigenvalues represented by the resulting (truncated) version of Eq. (14) accurately represent the experimental data, the resulting fitted set of $\{p_j\}$ coefficients cannot be expected to provide an optimum local representation of the effective potential function $V_{\text{eff}}(r)$ in the data-sensitive region. Rather, they comprise a set of non-physical model parameters which, within the (exact) Dunham algebra and the chosen truncation convention, yield a compact, accurate, internally consistent, and reproducible description of the experimental data. At the same time, exact eigenvalues of the Schrödinger equation containing the effective potential defined by that set of fitted potential coefficients cannot be expected to give an accurate representation of those experimental data. This is the source of the discrepancies illustrated by Table 1.

An alternate version of the conventional algebraic method which would avoid the types of discrepancies seen in Table 1 may also be readily implemented using program RADIATOM. For a case in which the potential function was defined by non-zero coefficients $c_0 - c_n$, this alternate approach would include in the summations of Eq. (14) all $Y_{l,m}$ and $Z_{l,m}^{A,B}$ coefficients which make non-negligible (relative to the experimental uncertainties) contributions to the observed level energies, and not merely those for which $2l + m - 2 \leq n$. This extended set of $Y_{l,m}$ values would, of course, still depend only on $c_0 - c_n$. Within the structure of RADIATOM this approach may be implemented by defining the cutoff of the sums over l and m by the condition $2l + m - 2 \leq j(\max)$ for some selected value of $j(\max) \geq n$, while fixing $c_j = 0$ for all $n < j \leq j(\max)$. If the truncation of the sums in Eq. (14) is indeed the source of the discrepancies in question, repeating the published RADIATOM analyses using successively larger values of $j(\max)$ should lead to convergence to the results of the numerical-method analyses. Tests of this thesis are presented below.

4. Testing our explanation for the discrepancies

The five molecular systems considered here are those listed in Table 1. The multi-isotopomer data sets (and uncertainties) were chosen to be as close as possible to those used in the corresponding published numerical- and algebraic-fit analyses, and details regarding their composition and the original sources of the data may be found in the references listed in Table 1. For these systems, Table 2 summarizes the results of a number of algebraic fits performed with RADIATOM using a range of choices for the parameter $j(\max)$ which controls the truncation of the sets of $\{Y_{l,m}\}$, $\{Z_{l,m}^A\}$, and $\{Z_{l,m}^B\}$ coefficients in Eq. (14). The column labeled “fitted” under the heading “highest-order potential coefficient” gives the value of the highest-order non-zero potential coefficient c_n determined in that fit, while the column labeled “algebra” under that same heading identifies the potential coefficient $c_{j(\max)}$ used to define the truncation of the $Y_{l,m}$ coefficients utilized in the analysis, according to the criterion that $2l + m - 2 \leq j(\max)$. For $j(\max) > n$ the values of coefficients $c_{n+1}, c_{n+2}, \dots, c_{j(\max)}$ are fixed at zero in the associated algebra. Similarly, under the group heading “highest-order BOB coefficient” in Table 2, the columns labeled “fitted by RADIATOM” list the values of the highest-order non-zero parameters for each type of Born–Oppenheimer breakdown function considered in that analysis, while the column labeled “algebra” indicates the orders of the parameters used to define the limits on the collections of $Z_{l,m}^A$ and $Z_{l,m}^B$ coefficients used in the analysis. Finally, the second-last column of this table gives the dimensionless root-mean-square deviation $\overline{dd}(\text{fit})$ of the RADIATOM-based algebraic fit for

each case, while the last column $\overline{dd}(\text{test})$ shows the average dimensionless residual yielded by a numerical-method simulation of the input data, performed using the parameters yielded by the associated RADIATOM fit. As $j(\max)$ increases, convergence of these $\overline{dd}(\text{test})$ values to agreement with both the associated $\overline{dd}(\text{fit})$ values and the corresponding numerical-fit results from Table 1 would confirm the validity of our explanation for the discrepancies between the published numerical- and (RADIATOM-based) algebraic-fit analyses.

For each of the five molecular systems considered in Table 2, case (i) corresponds to the literature comparison summarized in Table 1.⁵ The next three (for NaCl, GeS, and BrCl), two (for LiH) or one (for GaH) cases then show the effect of increasing $j(\max)$ and including more $\{Y_{l,m}\}$ coefficients in the representation of the energies $E_{v,j}$. In particular, for NaCl, BrCl, and GeS the fitted model potential was defined by the five potential parameters $c_0 - c_4$; in each case (i) fit the algebra therefore only took account of the 15 Dunham coefficients (including $Y_{0,1}$) corresponding to $\{l,m\}$ combinations lying above the dashed curve in Fig. 1, while in the case (iii) fits (“algebra” = c_8 , or $j(\max) = 8$) they also utilized the 20 additional coefficients associated with the interval between the dashed and dotted curves in Fig. 1. Note that the existing version of RADIATOM does not allow fully consistent extension of these simulations beyond the “algebra” = c_{10} limit (i.e., $j(\max) = 10$) for the potential, or beyond the $s_6^{A,B}$, $t_6^{A,B}$, and $u_6^{A,B}$ limits for the BOB terms [22,26].

For the NaCl data set, extending the algebraic treatment to include $Y_{l,m}$ coefficients corresponding to $j(\max) > 4$ quickly leads to convergence, as the value of $\overline{dd}(\text{test})$ already agrees with the numerical-fit result for the “algebra” = c_8 fit of case (iii). Case (v) then shows that extending the order of the algebra used to treat the fitted BOB parameter $t_0(\text{Cl})$ does not affect this conclusion, while case (vi) shows that this latter result is in any case almost irrelevant, since the quality of fit becomes marginally worse on neglect of all BOB terms. It is also noteworthy to see that as the sophistication of the algebraic treatment is extended, the value of the highest-order potential coefficient determined by the RADIATOM fit changes sign and comes into agreement with those yielded by the numerical (SSPOT) and DS-cP analyses of [32,36], $c_4(\text{SSPOT}) = 0.345(\pm 0.016)$ and $c_4(\text{DS-cP}) = 0.342(\pm 0.016)$. In other words, if the internal truncation is based on a sufficiently large value of $[j(\max) - n]$, where c_n is the highest-order non-zero potential coefficient, the conventional algebraic method can indeed yield essentially exactly the same potential

⁵ The minor differences between some $\overline{dd}(\text{fit})$ values in the two tables reflect the effect of rounding of the published parameter values.

Table 2
Results and tests of various fits performed using Ogilvie's algebraic method RADIATOM code

Case	Highest-order potential coefficient		Highest-order BOB coefficient		$\bar{d}d(\text{fit})$	$\bar{d}d(\text{test})$		
	Fitted	Algebra	Fitted by RADIATOM	Algebra				
NaCl	(i)	$c_4 = -0.258(19)$	c_4	$t_0^{\text{Cl}} = -1.42(29)$	—	t_0^{Cl}	0.906	16.222
	(ii)	$c_4 = 0.315(16)$	c_6	$t_0^{\text{Cl}} = -1.43(29)$	—	t_0^{Cl}	0.901	1.313
	(iii)	$c_4 = 0.340(16)$	c_8	$t_0^{\text{Cl}} = -1.42(29)$	—	t_0^{Cl}	0.920	0.924
	(iv)	$c_4 = 0.338(16)$	c_{10}	$t_0^{\text{Cl}} = -1.42(29)$	—	t_0^{Cl}	0.921	0.924
	(v)	$c_4 = 0.343(16)$	c_{10}	$t_0^{\text{Cl}} = -1.52(30)$	—	t_6^{Cl}	0.920	0.918
	(vi)	$c_4 = 0.342(16)$	c_{10}	—	—	—	0.930	0.922
	(vii)	$c_4 = 0.342(16)$	c_{10}	$u_1^{\text{Cl}} = -7.(3) \times 10^4$	—	u_6^{Cl}	0.928	0.923
GeS	(i)	$c_4 = -0.106(28)$	c_4	$s_0^{\text{Ge}} = 1.36(41)$	$t_0^{\text{Ge}} = -1.40(13)$ $t_0^{\text{S}} = -1.82(8)$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}$ t_0^{S}	0.948	4.799
	(ii)	$c_4 = -0.216(26)$	c_6	$s_0^{\text{Ge}} = 1.41(40)$	$t_0^{\text{Ge}} = -1.41(13)$ $t_0^{\text{S}} = -1.84(8)$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}$ t_0^{S}	0.930	1.074
	(iii)	$c_4 = -0.216(25)$	c_8	$s_0^{\text{Ge}} = 1.42(40)$	$t_0^{\text{Ge}} = -1.41(13)$ $t_0^{\text{S}} = -1.84(8)$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}$ t_0^{S}	0.930	1.038
	(iv)	$c_4 = -0.216(25)$	c_{10}	$s_0^{\text{Ge}} = 1.42(40)$	$t_0^{\text{Ge}} = -1.41(13)$ $t_0^{\text{S}} = -1.84(8)$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}$ t_0^{S}	0.930	1.042
	(v)	$c_4 = -0.206(25)$	c_{10}	$s_0^{\text{Ge}} = 1.51(41)$	$t_0^{\text{Ge}} = -1.42(13)$ $t_0^{\text{S}} = -1.85(8)$	$s_6^{\text{Ge}}, t_0^{\text{Ge}}$ t_0^{S}	0.928	0.928
	(vi)	$c_4 = -0.240(31)$	c_{10}	$u_2^{\text{Ge}} = 2.6(3) \times 10^6$	$u_1^{\text{S}} = -3.2(3) \times 10^5$	$u_6^{\text{Ge}}, u_6^{\text{S}}$	1.121	1.121
	(vii)	$c_4 = -0.204(26)$	c_{10}	$u_2^{\text{Ge}} = 3.1(3) \times 10^6$	$u_2^{\text{S}} = 3.3(2) \times 10^6$	$u_6^{\text{Ge}}, u_6^{\text{S}}$	0.930	0.930
BrCl	(i)	$c_4 = 4.05(4)$	c_4	$s_0^{\text{Br}} = 1.70(26)$ $s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Br}} = -0.49(10)$ $t_0^{\text{Cl}} = -0.65(2)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$ $s_0^{\text{Cl}}, t_0^{\text{Cl}}$	0.936	9.136
	(ii)	$c_4 = 2.23(4)$	c_6	$s_0^{\text{Br}} = 1.68(26)$ $s_0^{\text{Cl}} = 0.85(6)$	$t_0^{\text{Br}} = -0.52(10)$ $t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$ $s_0^{\text{Cl}}, t_0^{\text{Cl}}$	0.938	1.642
	(iii)	$c_4 = 2.16(4)$	c_8	$s_0^{\text{Br}} = 1.67(26)$ $s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Br}} = -0.52(10)$ $t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$ $s_0^{\text{Cl}}, t_0^{\text{Cl}}$	0.939	1.322
	(iv)	$c_4 = 2.15(4)$	c_{10}	$s_0^{\text{Br}} = 1.67(26)$ $s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Br}} = -0.52(10)$ $t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$ $s_0^{\text{Cl}}, t_0^{\text{Cl}}$	0.940	1.339
	(v)	$c_4 = 2.17(4)$	c_{10}	$s_0^{\text{Br}} = 1.73(27)$ $s_0^{\text{Cl}} = 0.86(6)$	$t_0^{\text{Br}} = -0.53(10)$ $t_0^{\text{Cl}} = -0.66(1)$	$s_6^{\text{Br}}, t_0^{\text{Br}}$ $s_6^{\text{Cl}}, t_0^{\text{Cl}}$	0.939	0.939
	(vi)	$c_4 = 2.15(4)$	c_{10}	$s_0^{\text{Br}} = 1.67(26)$ $s_0^{\text{Cl}} = 0.84(6)$	$u_1^{\text{Br}} = -1.7(3) \times 10^5$ $u_1^{\text{Cl}} = -2.1(1) \times 10^5$	$s_6^{\text{Br}}, u_6^{\text{Br}}$ $s_6^{\text{Cl}}, u_6^{\text{Cl}}$	0.940	0.940
	(vii)	$c_4 = 2.18(4)$	c_{10}	$u_2^{\text{Br}} = 1.3(2) \times 10^6$	$u_2^{\text{Cl}} = 1.25(4) \times 10^6$	$u_6^{\text{Br}}, u_6^{\text{Cl}}$	0.941	0.941
LiH	(i)	$c_6 = 0.040(10)$	c_6	$t_1^{\text{Li}} = 0.105(56)$ $t_2^{\text{H}} = -0.99(9)$	$u_1^{\text{Li}} = 1.21(1) \times 10^5$ $u_5^{\text{H}} = -1.3(3) \times 10^5$	$t_1^{\text{Li}}, u_5^{\text{Li}}$ $t_2^{\text{H}}, u_5^{\text{H}}$	1.103	41.10
	(ii)	$c_6 = -0.086(19)$	c_8	$t_1^{\text{Li}} = 0.062(56)$ $t_2^{\text{H}} = -0.86(9)$	$u_2^{\text{Li}} = 1.21(1) \times 10^5$ $u_5^{\text{H}} = -2.1(3) \times 10^5$	$t_1^{\text{Li}}, u_2^{\text{Li}}$ $t_2^{\text{H}}, u_5^{\text{H}}$	1.102	38.46
	(iii)	$c_6 = -0.040(26)$	c_{10}	$t_1^{\text{Li}} = 0.071(57)$ $t_2^{\text{H}} = -0.95(10)$	$u_2^{\text{Li}} = 1.21(1) \times 10^5$ $u_5^{\text{H}} = -1.7(3) \times 10^5$	$t_1^{\text{Li}}, u_2^{\text{Li}}$ $t_2^{\text{H}}, u_5^{\text{H}}$	1.111	40.21
	(iv)	$c_6 = -0.010(24)$	c_{10}	$t_1^{\text{Li}} = 0.072(79)$ $t_2^{\text{H}} = 0.042(90)$	$u_3^{\text{Li}} = 1.06(1) \times 10^5$ $u_5^{\text{H}} = -1.1(5) \times 10^5$	$t_6^{\text{Li}}, u_6^{\text{Li}}$ $t_6^{\text{H}}, u_6^{\text{H}}$	1.378	2.54
	(v)	$c_4 = -0.0418(3)$	c_{10}	$t_1^{\text{Li}} = 0.056(79)$ $t_2^{\text{H}} = -0.032(81)$	$u_2^{\text{Li}} = 1.06(1) \times 10^5$ $u_4^{\text{H}} = 1.1(1) \times 10^5$	$t_6^{\text{Li}}, u_6^{\text{Li}}$ $t_6^{\text{H}}, u_6^{\text{H}}$	1.392	4.173
	(vi)	$c_4 = -0.0425(2)$	c_{10}	$t_0^{\text{Li}} = 0.824(61)$ $t_3^{\text{H}} = 2.125(74)$	$u_3^{\text{Li}} = -1.4(1) \times 10^5$ $u_3^{\text{H}} = 1.9(1) \times 10^4$	$t_6^{\text{Li}}, u_6^{\text{Li}}$ $t_6^{\text{H}}, u_6^{\text{H}}$	1.057	1.588
GaH	(i)	$c_8 = -1.63(11)$	c_8	$t_3^{\text{Ga}} = 3.5(7)$ $t_3^{\text{H}} = 16.3(4)$	$u_5^{\text{Ga}} = 3.9(14) \times 10^5$ $u_6^{\text{H}} = -2.6(3) \times 10^6$	$t_1^{\text{Ga}}, u_3^{\text{Ga}}$ $t_2^{\text{H}}, u_6^{\text{H}}$	0.910	283.3
	(ii)	$c_8 = -0.19(2)$	c_{10}	$t_1^{\text{Ga}} = 2.4(7)$ $t_2^{\text{H}} = 14.0(4)$	$u_3^{\text{Ga}} = 4.5(13) \times 10^5$ $u_6^{\text{H}} = -1.4(3) \times 10^6$	$t_1^{\text{Ga}}, u_3^{\text{Ga}}$ $t_2^{\text{H}}, u_6^{\text{H}}$	0.854	36.53
	(iii)	$c_8 = -0.33(2)$	c_{10}	$t_1^{\text{Ga}} = 3.9(9)$ $t_3^{\text{H}} = 6.3(4)$	$u_3^{\text{Ga}} = -2.0(9) \times 10^5$ $u_6^{\text{H}} = 2.0(1) \times 10^6$	$t_6^{\text{Ga}}, u_6^{\text{Ga}}$ $t_6^{\text{H}}, u_6^{\text{H}}$	0.929	62.67
	(iv)	$c_8 = -0.18(2)$	c_{10}	$t_4^{\text{Ga}} = 6.0(8)$ $t_4^{\text{H}} = -10.3(3)$ $s_0^{\text{H}} = -0.81(4)$	$u_6^{\text{Ga}} = 1.6(2) \times 10^4$ $u_2^{\text{H}} = 6.9(2) \times 10^4$	$t_6^{\text{Ga}}, u_6^{\text{Ga}}$ $t_6^{\text{H}}, u_6^{\text{H}}$ s_6^{H}	0.887	8.858

Numbers in parentheses are one standard error uncertainties in the last digits shown for each fitted parameter. Quoted coefficients u_i^A have units cm^{-1} ; all others are dimensionless.

function parameters as the numerical and DS-cP methods.

For GeS and BrCl, the results for cases (i)–(iv) show that even when the RADIATOM algebra is pushed to its current limit (“algebra” = c_{10} , or $j(\max) = 10$) with regard to extension of the $Y_{l,m}$ sums, full convergence of $\overline{dd}(\text{test})$ to the numerical-fit result of Table 1 is not achieved. However, complete convergence is achieved when the algebraic treatment of the $\{Z_{l,m}^{A,B}\}$ coefficients is also extended to the limit allowed by the program, case (v). Note that the resulting fitted c_4 values for case (v) also now agree with those yielded by the numerical-fit analysis of [36], while differing from those yielded by the published [case (i) type] RADIATOM analyses [29,30] by factors of two. This again shows that if $[j(\max) - n]$ is sufficiently large, RADIATOM analyses can yield the same potential energy function obtained from numerical-fit analyses. The results for cases (vi) and (vii) (see Section 6) also show that this full convergence may also be achieved when using other choices for the selection of BOB parameters to be determined by the fits.

The results of applying the extended RADIATOM algebra analysis to the LiH molecule data set are not as straightforward as those for the heavy-molecule cases discussed above. In particular, the $\overline{dd}(\text{test})$ values in Table 2 show that merely extending the $Y_{l,m}$ algebra to the “algebra” = c_{10} limit [case (iii)] gives no improvement in the quality of the resulting model. In contrast, the results for case (iv) show that also extending the algebraic treatment of the $\{Z_{l,m}^{A,B}\}$ coefficients as far as possible gives a model whose predictions are only 2.3 (rather than 38!) times worse than the numerical- and DS-cP-fit result seen in Table 1 [35]. However, the uncertainties in the resulting highest-order t_j parameters and in the two highest-order potential parameters yielded by this case (iv) fit (Table 2, and $c_5 = -0.0005(\pm 0.011)$) are all greater than 100%. This implies that this data set does not really require the seven potential coefficients used in the RADIATOM analyses of [3,31]. This conclusion is consistent with the fact that the numerical- and DS-cP-fits of [35] were able to obtain good fits to this data set using only the five potential parameters $c_0 - c_4$.

The last two LiH cases presented in Table 2 examine the question of whether potential coefficients c_5 and c_6 are actually needed, by combining fits to a potential function defined only by $c_0 - c_4$ with two choices for the BOB function parameter sets. Case (v) uses a slightly truncated version of the set of BOB parameters fitted in the original [case (i)] RADIATOM analysis of Ogilvie [31],⁶ while case (vi) is based on the same BOB parameter set used in the numerical- and DS-cP-fit analyses of [35]. As far as RADIATOM is concerned, the quality of the case (iv) and case

(v) fits is the same; i.e., the similarity of the $\overline{dd}(\text{fit})$ values for these two cases indicates that when the algebra is extended, RADIATOM is not sensitive to the presence of c_5 and c_6 coefficients. However, the large $\overline{dd}(\text{test})$ values and the fact that the highest-order fitted t_j coefficients for case (v) have uncertainties greater than 100% shows that it is not a good model. Thus, it appears that it was only the early truncation of the sets of $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients used by RADIATOM which made the published analyses of [3,31] appear to require the presence of potential function coefficients c_5 and c_6 .

Case (vi) is clearly the best of the RADIATOM-analysis models for LiH considered here, in that it gives the lowest values of both $\overline{dd}(\text{fit})$ and $\overline{dd}(\text{test})$. The former indicates that the set of internal Dunham-type coefficients generated by the algebra represents the data as well as the best of any of the published analyses. However, the associated value of $\overline{dd}(\text{test})$ is still 50% larger than the values attained in the numerical- and DS-cP-fit analyses. This shortcoming is almost certainly due to the limitations on the orders of the algebra implemented in the current version of the RADIATOM code, and if its treatment of the $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients could be extended to higher order, complete agreement with the numerical-fit results could be expected. This argument is supported by the close agreement between the values of the potential energy and other radial function parameters obtained for case (vi) (not shown here) and those reported in the potential-fit analysis of [35].

The final system considered here, GaH, is a particularly challenging one, in that the published RADIATOM, numerical-fit, and DS-cP-fit analyses all agree that some nine potential parameters $c_0 - c_8$ and several BOB radial function parameters for each atom are required by any model which can adequately describe the given data set [3,27,37]. As a result, our case (i) starting point is quite close to the upper bound on the order of the algebraic treatment allowed by the current version of RADIATOM ($j(\max) = 10$ for potential coefficients and $j(\max) = 6$ for the BOB radial functions). Thus, although extending the algebraic treatment of the $\{Y_{l,m}\}$ coefficients to the “algebra” = $c_{10}(j(\max) = 10)$ limit implemented in RADIATOM does reduce the value of $\overline{dd}(\text{test})$ by a factor of eight [case (ii)], if we also extend the algebraic treatment of the $\{Z_{l,m}^{A,B}\}$ coefficients as far as possible [case (iii)], it actually makes the agreement worse. Utilizing the alternate selection of Born–Oppenheimer breakdown radial function parameters used in [37] in place of that of [27] does help [case (iv)], but the result is still far from satisfactory. As a result, the best potential energy and BOB radial functions obtainable with the existing version of the RADIATOM program yield eigenvalue differences which disagree with experiment by (on average) an order of magnitude more than the experimental uncertainties. Once again, however, we believe that this result is not an inherent limitation of the algebraic method,

⁶ The u_5^H parameter was omitted, since it seemed inappropriate to include it when there is no c_5 term in the potential function.

but rather reflects the limitation on the numbers of consistent $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients which can be generated in the current RADIATOM implementation. At the same time, it is important to realize that the small values of $\overline{dd}(\text{fit})$ obtained for all of these cases indicate that the truncated sets of $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients generated within the RADIATOM procedure do provide fully satisfactory empirical representations of the data.

In summary, therefore, the convergence of the $\overline{dd}(\text{test})$ values achieved on proceeding from case (i) to case (v) for the first three molecular systems considered in Table 2, as well as the analogous substantial improvements obtained for the hydride systems, confirm that the disagreement between published numerical- and algebraic-fit analyses for various molecules is indeed due to the ‘‘Ogilvie truncation convention’’ used in published RADIATOM-based applications of the algebraic-fit method. In contrast, results obtained by Molski using his algebraic DS-cP method were generally quite satisfactory—yielding small $\overline{dd}(\text{test})$ values and potential energy and adiabatic and non-adiabatic radial function parameters in good agreement with those determined from numerical-method fits for all of the cases considered here [35–37]. This difference reflects the fact that Molski apparently extended the Dunham algebra to include quite high order $Y_{l,0}^{(v,j)}$ coefficients, while all published RADIATOM applications were based on the convention of ignoring all $Y_{l,m}$ coefficients which depend in part on potential expansion coefficients c_j not determined by the analysis. In contrast, although *within* the RADIATOM program they yield sets of $Y_{l,m}$ and $Z_{l,m}^{A,B}$ coefficients which accurately reproduce the input experimental data, the radial functions reported in all published RADIATOM-based applications of the algebraic method do not yield optimum descriptions of the potential energy and BOB radial functions on the interval spanned by the experimental data.

In spite of the above, the present study shows that the conventional algebraic method itself is fundamentally valid, in that when the internal algebra is extended to utilize sufficiently large numbers of $Y_{l,m}$ and $Z_{l,m}^{A,B}$ coefficients, it can yield potential energy and BOB radial functions in full agreement with the numerical-fit method. However, in contrast with the DS-cP method [35,37], the results in Table 2 show that the limits allowed by its current implementation prevents the RADIATOM program from providing satisfactory descriptions of systems for which relatively high order radial function parameters are required in the analysis.

5. Can the algebraic method generate reliable $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients from a known potential?

The preceding discussion focussed attention on problems encountered in determining potential energy and

BOB functions from fits to experimental data. Another possible use for the ‘‘Dunham algebra’’ implemented in the RADIATOM program would be to generate sets of accurate $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ level-energy expansion coefficients for a known potential energy function expanded in the power series form of Eq. (9). However, such applications encounter the same algebraic convergence difficulties discussed above. The results in Table 3 show how those convergence problems affect ‘‘forward’’ calculations of eigenvalues using Dunham expansion coefficients generated from specified potential energy and BOB function parameters for the five molecular systems considered above.

For the same five molecular data sets considered earlier, the parameters defining the potential energy and BOB functions determined from the numerical direct-potential-fit data analyses of [35–37] were input into RADIATOM. The program then generated sets of internal $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients, which in turn were used to predict the transition energies on which the original numerical-fit analyses were based. The ratio of the dimensionless root mean square deviation associated with these predictions, to the those for the published numerical fit (see Table 1), $\overline{dd}(\text{algebra})/\overline{dd}(\text{num. fit})$, then provides a measure of the adequacy of those sets of internal $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients. As discussed in Sections 3 and 4, for a potential defined by non-zero parameters $c_0 - c_n$, RADIATOM may be set to generate only $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients which depend on non-zero potential energy and BOB function parameters ($j(\text{max}) = n$), or it can be required to generate higher-order coefficients as well by setting $j(\text{max}) > n$. The results shown in Table 3 were obtained by truncating the sets of $\{Y_{l,m}\}$ coefficients so that case ‘‘algebra = $c_{j(\text{max})}$ ’’ takes account of all $Y_{l,m}$ coefficients for which $2l + m - 2 \leq j(\text{max})$. The associated treatment of adiabatic and non-adiabatic radial function parameters considered only the two cases: (a) use only those $Z_{l,m}^A$ and $Z_{l,m}^B$ coefficients which depend *only* on the non-zero BOB-function parameters of the model, or (b) generate all coefficients possible within the current (algebra = $s_6^{A,B}$, $t_6^{A,B}$, and/or $u_6^{A,B}$) technical limit of the RADIATOM program.

The results in Table 3 follow the pattern seen in Table 2: as the numbers of $Y_{l,m}$ and $Z_{l,m}^{A,B}$ expansion coefficients used for a given system is increased by increasing $j(\text{max})$, the accuracy of the simulation improves. For the three heavy-atom cases NaCl, GeS, and BrCl, this convergence brings the predictions into full agreement with experiment. For the hydrides, however, we see once again that although extending the algebra yields substantially improved agreement, fully satisfactory predictions cannot be generated because of the current technical limitations of the RADIATOM code. Overall, these results show that even with the best program currently available, truly reliable sets of $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients can only be generated for potential energy

Table 3

Tests of predictions yielded by $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ coefficients generated algebraically from numerical-fit potential energy and other radial functions

Case	Highest potential coefficient		Highest-order BOB coefficient		$\overline{dd}(\text{algebra})/\overline{dd}(\text{num. fit})$	
	In fit	Algebra	In the fit	In the algebra		
NaCl	(i)	c_4	c_4	t_0^{Cl}	t_0^{Cl}	5.17
	(ii)	c_4	c_6	t_0^{Cl}	t_0^{Cl}	1.37
	(iii)	c_4	c_8	t_0^{Cl}	t_0^{Cl}	1.01
	(iv)	c_4	c_{10}	t_0^{Cl}	t_0^{Cl}	1.01
	(v)	c_4	c_{10}	t_0^{Cl}	t_6^{Cl}	1.00
GeS	(i)	c_4	c_4	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	4.83
	(ii)	c_4	c_6	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	1.16
	(iii)	c_4	c_8	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	1.12
	(iv)	c_4	c_{10}	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	1.12
	(v)	c_4	c_{10}	$s_0^{\text{Ge}}, t_0^{\text{Ge}}, s_0^{\text{S}}$	$s_6^{\text{Ge}}, t_6^{\text{Ge}}, s_6^{\text{S}}$	1.00
BrCl	(i)	c_4	c_4	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	15.23
	(ii)	c_4	c_6	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	1.78
	(iii)	c_4	c_8	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	1.46
	(iv)	c_4	c_{10}	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	1.45
	(v)	c_4	c_{10}	$s_0^{\text{Br}}, s_0^{\text{Cl}}, t_0^{\text{Br}}, t_0^{\text{Cl}}$	$s_6^{\text{Br}}, s_6^{\text{Cl}}, t_6^{\text{Br}}, t_6^{\text{Cl}}$	1.00
LiH	(i)	c_4	c_4	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	171.59
	(ii)	c_4	c_6	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	25.08
	(iii)	c_4	c_8	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	24.03
	(iv)	c_4	c_{10}	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	24.03
	(v)	c_4	c_{10}	$t_0^{\text{Li}}, t_3^{\text{H}}, u_3^{\text{Li}}, u_3^{\text{H}}$	$t_6^{\text{Li}}, t_6^{\text{H}}, u_6^{\text{Li}}, u_6^{\text{H}}$	2.19
GaH	(i)	c_8	c_8	$s_0^{\text{H}}, t_1^{\text{Ga}}, t_4^{\text{H}}, u_1^{\text{Ga}}, u_2^{\text{H}}$	$s_0^{\text{H}}, t_1^{\text{Ga}}, t_4^{\text{H}}, u_1^{\text{Ga}}, u_2^{\text{H}}$	689.19
	(ii)	c_8	c_{10}	$s_0^{\text{H}}, t_1^{\text{Ga}}, t_4^{\text{H}}, u_1^{\text{Ga}}, u_2^{\text{H}}$	$s_0^{\text{H}}, t_1^{\text{Ga}}, t_4^{\text{H}}, u_1^{\text{Ga}}, u_2^{\text{H}}$	660.86
	(ii)	c_8	c_{10}	$s_0^{\text{H}}, t_1^{\text{Ga}}, t_4^{\text{H}}, u_1^{\text{Ga}}, u_2^{\text{H}}$	$s_6^{\text{H}}, t_6^{\text{Ga}}, t_6^{\text{H}}, u_6^{\text{Ga}}, u_6^{\text{H}}$	9.07

and adiabatic and non-adiabatic radial functions involving a modest number of expansion parameters. At the same time, the results in Table 3 further confirm that the discrepancy between published algebraic-fit and numerical-fit data analyses was in fact due to the truncation convention used in published RADIATOM-based analyses.

6. Can dipole moments and rotational g factors be determined from transition energy data alone?

A more recent controversy in this area concerns the question of whether or not electrical properties of a heteronuclear diatomic molecule—its dipole moment and rotational g -factor—could be determined from transition energy data obtained in the absence of external fields. The central question in this regard is whether or not unique values of t_0^A and t_0^B , the leading coefficients of the expansions representing the two atom-specific radial functions $R^A(r)$ and $R^B(r)$ which combine to yield the centrifugal BOB function $\alpha(r)$ of Eqs. (2) and (6), could be determined reliably from such data. One view was that this could be done, and a number of data analyses supporting this position have been published [3,29–31,69]. On the other hand, according to the alternate version of Eq. (6) derived by Watson, the effects of the

$Q^A(r)$ and $Q^B(r)$ kinetic-energy and $R^A(r)$ and $R^B(r)$ centrifugal BOB functions can not be distinguished from those of the adiabatic potential energy functions $S^A(r)$ and $S^B(r)$ [43,45,70]. This implies that unique values of t_0^A and t_0^B , and hence of the dipole moment and rotational g -factor, cannot be determined from transition energy data alone.

This negative conclusion is supported by the form of the expressions for $Z_{l,m}^{A,B}$ coefficients listed in Tables 4.17 and 4.18 of [3], which show that the low-order coefficients depend on combinations of $\{s_j^{A,B}\}$, $\{t_j^{A,B}\}$, and $\{u_j^{A,B}\}$ expansion parameters in a way which would prevent unique determination of individual coefficient values, or at least prevent it until very high order sets of empirical $Z_{l,m}^{A,B}$ coefficients were accurately determined. The fact that all of the data analyses claiming to determine these factors utilized very low-order expansion in the BOB radial function parameters indicates that Watson is certainly correct, at least for those cases. The results of the present RADIATOM analyses for GeS and BrCl shown in Table 2 also clearly support Watson's conclusion. In particular, his derivations [45,70] show that the BOB parameters t_0^A and u_1^A both contribute additively to the same $Z_{l,m}^A$ correction coefficients, which implies that they cannot be determined independently. This conclusion is supported by independent physical arguments [48], and by comparison of the present case (v)

and case (vii) results for GeS and BrCl. In particular, although the values of t_0^A and t_0^B yielded by the case (v) fits appear to be statistically significant (i.e., having uncertainties $<100\%$), the fact that fits of equivalent quality are obtained when those parameters were fixed at zero and the parameters u_1^A varied in the fits shows that conclusion was an artifact of the choice of model Hamiltonian and the limited number of correction function coefficients considered. Similarly, although the NaCl RADIATOM analysis of [32] [our case (i)] yielded an apparently moderately well determined value of t_0^{Cl} (uncertainty $\pm 20\%$), the present results for cases (v)–(vii) of Table 2 show that essentially the same quality of fit is obtained if the one BOB function parameter varied was u_1^{Cl} , or indeed if the model included no BOB function parameters at all.

While fully satisfactory RADIATOM analyses are not possible for LiH and GaH because of limitations of the current version of the code, within the statistics of the RADIATOM fits themselves we find that the quality of fit in no way indicates that unique physically significant values of t_0^A may be determined. In particular, if the LiH fits of cases (i), (iv), and (vi) in Table 2 are repeated while fixing $t_0^{\text{Li}} = t_0^{\text{H}} = 0$, the resulting values of $\overline{\text{dd}}(\text{fit})$ are 1.154, 1.174, and 1.076, respectively, value essentially equivalent to those for the best fits in which t_0^{Li} and t_0^{H} were varied. Similarly, repeating the RADIATOM fit for GaH corresponding to case (iii) while fixing $t_0^{\text{Ga}} = t_0^{\text{H}} = 0$ (but allowing u_2^{H} to vary) yielded $\overline{\text{dd}}(\text{fit}) = 0.902$, a value even *smaller* than that for case (iii). Thus, even for these incompletely converged LiH and GaH cases, RADIATOM analyses confirm that unique independent values of t_0^A and t_0^B , and hence reliable estimates of dipole moments and rotational g -factors, *cannot* be determined from field-free transition energy data alone.

7. Conclusions

The main conclusions of the present work are the following:

(1) If the algebra incorporates *all* coefficients $Y_{l,m}$ and $Z_{l,m}^{A,B}$ which have non-negligible effects on the predicted transition energies, the conventional RADIATOM-type algebraic-fit method will yield the same results as a numerical fit using the same model potential energy and BOB functions.

The results obtained herein for the NaCl, GeS, and BrCl systems show that satisfactory convergence of the conventional algebraic method to yield potential energy and BOB function parameters in agreement with numerical-fit results can be achieved. However, the residual difficulties with the LiH and GaH systems indicate that this convergence will not be trivial to achieve for cases in which relatively high-order potential energy and BOB

function parameters are required. Moreover, the rapid growth of the computational effort associated with higher-order applications of the algebraic method may tend to make it unattractive to use when very high-order expressions are required [22]. On the other hand, the convergence of the conventional algebraic-fit method to agreement with the numerical-fit method with increasing values of the truncation index $j(\text{max})$ clearly removes any doubts which this longstanding dispute may have raised about the fundamental validity and utility of the direct-potential-fit approach to data analysis.

(2) The potential energy and BOB function parameters reported in all published RADIATOM-based analyses are effective internal parameters which can accurately represent the data within the “Ogilvie truncation convention” model, but they are not expected to yield reliable predictions when used to define the potential energy and BOB functions in the radial Schrödinger equation.

In all published RADIATOM-based analyses, the sets of internal Dunham coefficients $\{Y_{l,m}(\{c_j\})\}$ used in the analysis were truncated by neglecting all coefficients for which $2l + m - 2 > n$, where c_n was the highest-order non-zero potential expansion parameter in the model, and analogous truncation procedures were imposed for the atomic-mass-dependent BOB functions. This is a well-defined rule which yields a particularly compact set of intermediate $\{Y_{l,m}\}$ parameters for representing the experimental data. However, the leading Dunham coefficients $Y_{l,m}$ with $2l + m - 2 > n$ are mainly comprised of terms depending only on these those low-order potential energy parameters $c_0 - c_n$, and they can contribute significantly to calculated level energies. Thus, while fitting to data using this truncation convention certainly can yield a set of effective $\{Y_{l,m}\}$ coefficients which provide an accurate description of the experimental data within the assumptions of that model, the associated potential energy and BOB radial function parameters are not expected to provide optimum descriptions of those radial functions on the interval spanned by the input data. Moreover, comparison of the case (i) vs. case (vi) LiH results in Table 2 shows that a RADIATOM analysis using the Ogilvie truncation convention may require more potential function parameters than either more fully converged algebraic analyses or ones using numerical-fit or Molski's DS-CP methods.

Another perspective on the appropriateness of the “Ogilvie truncation convention” is provided by consideration of a hypothetical data set consisting of extensive highly accurate IR and MW data for a molecule whose potential energy curve is precisely described as a perfect harmonic oscillator. For such a system the exact quantum mechanical values of the inertial rotational constants B_v and of all centrifugal distortion constants

(CDCs) increase monotonically (in magnitude) with v .⁷ However, using the Ogilvie truncation convention, a RADIATOM analysis of such data which considered only the harmonic potential coefficient c_0 would only allow use of the Dunham coefficients $Y_{1,0}$, $Y_{0,1}$, and $Y_{0,2}$ for describing the level energies. This would neither allow for vibrational dependence of the rotational constants nor for the existence of higher-order CDC's, and hence would be unable to give an accurate fit to the given vibration–rotational data set.

(3) For cases in which there exist no published data analyses performed using other methods, published data analyses performed using RADIATOM should be repeated, since the input experimental data cannot be reproduced from the information presented in those papers.

While published RADIATOM-based analyses do yield compact internally consistent sets of radial-function parameters determined from the data, [35–37] show that when the associated potential energy and BOB functions are used in conventional Schrödinger-solver programs, they do not accurately reproduce the input data. The present paper explains why this occurs. Moreover, most published RADIATOM-based analyses do not report the sets of effective internal $\{Y_{l,m}\}$ and $\{Z_{l,m}^{A,B}\}$ parameters which actually do reproduce the data. Since program RADIATOM is not publicly available, readers wishing to reproduce or interpolate over the experimental data using the published parameters must either write their own version of that code, or adapt the early version of it reported in [22] which does not allow for BOB terms. Moreover, since the “Ogilvie truncation conventions” which are the source of the discrepancies examined herein are not explicitly presented in the literature (prior to this work), and are not implemented in the code presented in [22], a reader attempting to construct an equivalent algebraic-method code would have had difficulty doing so.

(4) Most applications of the DS-cP version of the algebraic method developed by Molski have not suffered from the truncation problems referred to above, and numerical simulation tests of the sets of potential energy and BOB functions determined by his method generally yield results in excellent agreement with the experimental data.

(5) Tests performed here confirm that claims to have obtained reliable dipole moments and rotational g -factors from analyses of transition energy data alone were incorrect.

In closing, we note that this whole discussion has been focussed on the simple power-series potential energy and BOB functions of Eqs. (9)–(12), because the

algebraic methods can only be directly applied to functions of that type. However, because of their generally inappropriate and often unphysical long-range behaviour, such functions cannot be applied readily in cases for which the experimental data span a very large fraction of the potential energy well, or if one wishes to be able to make reasonable predictions of properties outside the range of data used in the analysis, such as collisional properties of the atoms forming the molecule. The present work does show that when properly converged, the conventional algebraic-fit method is just as good as numerical-fit methods for direct-potential-fit data analyses using simple polynomial potential function models. However, its restriction to potentials expressed as simple power series will tend to limit its practical utility.

Acknowledgments

I am grateful to Dr. John Ogilvie for providing me with the initial versions of the data sets used in this study, for providing me with a copy of his program RADIATOM and answering questions regarding its use, and for stimulating discussions about the contents of the manuscript. I am also very grateful to Professor John Coxon for helpful discussions, and in particular for his performing the calculations which yielded the results in the last column of Table 2. I am also pleased to thank Professors Peter Bernath and Fred McCourt for their comments on the manuscript, and to Dr. Michael Dulick for helpful suggestions. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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⁷ Values of B_v would increase with v because the fact that the square of the wavefunction $|\psi_{v,0}(r)|^2$ is symmetric about r_e means that expectation values of $1/r^2$ will be dominated by contributions on the interval $r < r_e$.

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