Symbolic Computation in Molecular Spectroscopy

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Abstract: We demonstrate how to employ Maple for symbolic computations related to the analysis of pure rotational and vibration-rotational spectra of a simple diatomic molecular compound. We derive empirical relations that reproduce the main features of such band spectra and some combination relations employed to deduce values of band parameters from fitting frequencies of assigned lines. In a second section we generate expressions for vibration-rotational energies in terms of parameters in Dunham's function for potential energy. In both cases we indicate how these calculations are readily extensible as required for analysis of molecular spectra at the frontier of current research.

Introduction

In courses of physical chemistry and molecular physics within an undergraduate curriculum, the spectra of diatomic molecules serve a purpose to introduce students both to basic principles of molecular spectroscopy and to methods of treating physical problems. A diatomic molecule is a sufficiently simple system that a model can be examined analytically; the results therefrom are directly applicable to spectra that students record and analyze in a teaching laboratory. An instructor commonly presents on a blackboard a method with an approximation of low order, even though the results obtained are inadequate for quantitative analysis of the spectra produced on instruments currently available in typical laboratories. Algebraic complications of calculations to requisite greater orders preclude their being presented in class; it might be considered even unreasonable for students to be obliged to solve correctly by only manual means outside class these essentially algebraic problems. Software for symbolic computation, such as Maple, can naturally assist both instructors and students to develop a treatment to an order sufficiently high without tedious labour prone to error.

Here we consider a treatment of molecular spectra of diatomic molecules in two stages. First we develop a systematic approach, based on only empirical observations, to yield relations that a student employs in the course of analysis of laboratory spectra to derive spectral parameters of gaseous samples. In the second stage we demonstrate how a model is incorporated into the analysis to relate the spectral parameters to structural information that is chemically and physically meaningful. In both cases, the treatment is based on truncated power series; these are approximations to functions that cannot be determined analytically. They can be made as accurate as desired within some defined range; the fact that they diverge outside that range is irrelevant for the primary applications.

Processors for symbolic computing are especially suitable to handle truncated power series. The principal operations involved are series arithmetic, series reversion, differentiation and numerous substitutions. Although the series are computed to a low order (e.g. typically up to the sixth power), the coefficients typically involve several parameters; hence arithmetic with formulae is essential. Simplification and rearrangement of formulae is important in order to present results in the most meaningful way. Moreover, one seeks to use the formulae computed with a symbolic processor in other software such as Fortran; thus another operation for which Maple is useful is to convert formulae without error into Fortran code.

In the following two major sections of this paper we present Maple code, with a running commentary, that generates formulae that a student can employ to analyze laboratory spectra. In order to follow steps in the calculations, students will have seen the method worked by hand to low order, and will have been led through the code corresponding to those steps. Most current textbooks of physical chemistry and molecular physics contain, with expanded discussion, material for which the development in the first section is directly pertinent. Because of algebraic complications of Dunham's treatment of rotational and vibrational spectra of a diatomic molecule [1], to which the second section is devoted, few textbooks even on molecular spectroscopy describe it in detail, although in various extensions it remains the common basis for analysis of diatomic molecular spectra in current research [2, 3], and although analytic results from that treatment are more commonly presented. When tedious operations of the requisite algebra and calculus are undertaken symbolically with a computer, a student is freed to gain insight into the underlying physical concepts, beyond crudely simplified or inapplicable models, without the pain of manual work.

Development of Empirical Relations

We consider first a pure rotational spectrum of a simple diatomic molecular species that might be recorded in absorption in the far infrared or microwave spectral region. The most obvious feature of what one observes in such a spec-

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trum is a sequence of nearly equally spaced lines. For later convenience we denote by $2B$ the interval between adjacent lines. We here assume (although experiments readily prove) that the line at least frequency takes the molecule from the rotational state of least energy to the next state, and that successive lines in the sequence involve transitions only between adjacent states. With such an interval $2B$ between adjacent lines, the difference of energy between states is therefore $2B, 4B, 6B$, etc. The energies of the states are accordingly $0, 2B, 6B, 12B$, etc. We label each rotational state with a quantum number J that takes a value of only a non-negative integer; the state of least energy is thus identified with $J = 0$. We seek a relation between J and the energy of state J. For this purpose we fit a quadratic form to the first three states, and afterwards test this approach for all states.

We define $f(J)$ to be a quadratic form with coefficients a, b, c. In the Maple code below f is a function of J.

```
> f := J ->  B*(a*J^2+b*J+c);
```

$$f := J \to B\,(a\,J^2 + b\,J + c)$$

We set $f(J)$ equal to the known values $2B, 6B$ and $12B$ for $J = 1, 2, 3$, and solve the resulting linear equations for a, b, c.

```
> e1 := 2*B = f(1);
```

$$e1 := 2\,B = B\,(a + b + c)$$

```
> e2 := 6*B = f(2);
```

$$e2 := 6\,B = B\,(4\,a + 2\,b + c)$$

```
> e3 := 12*B = f(3);
```

$$e3 := 12\,B = B\,(9\,a + 3\,b + c)$$

```
> sols := solve( {e1,e2,e3}, {a,b,c} );
```

$$sols := \{a = 1, b = 1, c = 0\}$$

```
> f := subs( sols, f(J) );
```

$$f := B\,(J^2 + J)$$

For convenience we convert the above formula into a function of J.

```
> F := unapply(f,J);
```

$$F := J \to B\,(J^2 + J)$$

We test $J = 4$; we should obtain $20B$

```
> F(4);
```

$$20\,B$$

To prove that the quadratic form is correct for all energies, we use induction on J. Thus we assume that the polynomial is correct for $J = n$, that is, $F(n) = B(n^2 + n)$, and try to show that it is true for $J = n + 1$. We should have that

```
> F(n+1) = F(n) + 2*B*(n+1);
```

$$B\,\left((n+1)^2 + n + 1\right) = B\,(n^2 + n) + 2\,B\,(n+1)$$

```
> simplify(");
```

$$B\,(n^2 + 3\,n + 2) = B\,n^2 + 3\,B\,n + 2\,B$$

In fact, the value c=0 deduced above is not unique: any finite value of c satisfies the conditions; indeed in the early days of molecular spectroscopy the value c=1/4 was assumed, making $F(J) = B(J + \frac{1}{2})^2$. At present the form deduced above, with c=0, is almost invariably used.

On closer examination of the spectrum we discern that the interval between adjacent lines is not quite equal but decreases slowly as J increases. To take into account this behaviour we introduce corrections in the form of a polynomial of argument $J(J+1)$, using as many terms as are required to fit the available data. For historical reasons the coefficients of successive terms are denoted D, H, L, M..., with rapidly decreasing magnitudes. The Maple function F below takes as input a list of coefficients starting with B.

```
> F := (J,C) -> sum( C[i]*(J*(J+1))^i,
>                     i=1..nops(C) );
```

$$F := (J, C) \to \sum_{i=1}^{\mathrm{nops}(C)} C_i\,(J\,(J+1))^i$$

Here is the third-order approximation.

```
> F( J, [B,-D,H] );
```

$$B\,J\,(J+1) - D\,J^2\,(J+1)^2 + H\,J^3\,(J+1)^3$$

We assumed above that transitions occur between adjacent states; the appropriate short designation of that phenomenon is $\Delta J = +1$. Then we consider our sequence of lines to constitute a branch, called in this case the R branch. The definition of $R(J)$ follows.

```
> R:=(J,C)  -> collect(F(J+1,C)  - F(J,C), J):
> R(J,[B,-D]);
```

$$-4\,D\,J^3 - 12\,D\,J^2 + (2\,B - 12\,D)\,J + 2\,B - 4\,D$$

From experience we find that the most elegant representation of $R(J)$ is a series in $J + 1$ to only odd powers. To write $R(J)$ in this form in Maple we expand $R(J)$ as a Taylor series about $J = -1$.

```
> taylor(",J=-1,10);
```

$$2\,B\,(J+1) - 4\,D\,(J+1)^3$$

It is known that the interval between adjacent lines decreases, and that the lines converge to a finite limit called the *band head*. At that point the energy change from one state to the next becomes a maximum: thus $\frac{\mathrm{d}R(J)}{\mathrm{d}J} = 0$. Continuing with Maple we obtain

```
> Rhead := diff(convert(",polynom),J);
```

$$Rhead := 2\,B - 12\,D\,(J+1)^2$$

```
> sols := [solve(Rhead,J)];
```

$$sols := \left[-\frac{1}{24}\,\frac{24\,D+4\,\sqrt{6}\,\sqrt{D\,B}}{D},\; -\frac{1}{24}\,\frac{24\,D-4\,\sqrt{6}\,\sqrt{D\,B}}{D} \right]$$

```
> expand(");
```

$$\left[-1-\frac{1}{6}\,\frac{\sqrt{6}\,\sqrt{D\,B}}{D},\, -1+\frac{1}{6}\,\frac{\sqrt{6}\,\sqrt{D\,B}}{D} \right]$$

Because the second solution is positive, we select it, and test that it is indeed a maximum

```
> subs( J=" [2], diff(Rhead, J));,
```

$$-4\sqrt{6}\sqrt{DB}$$

The last line in the spectrum is actually characterised with an integer, to which the above solution is an approximation. One can obtain an analytic solution for the value of J at the band head even when one takes an additional term in the expansion $R(J)$, as follows.

```
> R(J,[B,-D,H]);
```

$$6\,H\,J^5+30\,H\,J^4+(\,-4\,D+62\,H\,)\,J^3 + (\,66\,H-12\,D\,)\,J^2+(\,2\,B+36\,H-12\,D\,)\,J + 2\,B-4\,D+8\,H$$

```
> solve(diff(Rhead,J),J);
```

$$-1+\frac{1}{30}\sqrt{30}\sqrt{\frac{-3\,H+6\,D+\%1}{H}},\quad -1-\frac{1}{30}\sqrt{30}\sqrt{\frac{-3\,H+6\,D+\%1}{H}},\quad -1+\frac{1}{30}\sqrt{-\frac{90\,H-180\,D+30\,\%1}{H}},\quad -1-\frac{1}{30}\sqrt{-\frac{90\,H-180\,D+30\,\%1}{H}}$$

$$\%1 := \sqrt{36\,D^2-36\,H\,D+9\,H^2-60\,H\,B}$$

By inspection the meaningful solution is the first one here. When one obtains numerical values for B, D and H, one discovers that similar values of J at the band head result from the two approximations.

We proceed to expand the treatment to include two vibrational states, each of which has an associated manifold of rotational states. We neglect for the moment the vibrational energy and focus on the two branches of lines normally present in the absorption spectrum of our simple diatomic species. The R branch, as before, denotes transitions in a series with $\Delta J = +1$, but we have also a P branch corresponding to $\Delta J = -1$. The Maple procedures below generate the series of transitions for these branches.

```
> R := (J,CU,CL)  ->   F(J+1,CU)  - F(J,CL):
> P := (J,CU,CL)  -> F(J-1,CU)  - F(J,CL):
```

The parameters CU and CL specify the coefficients of $J(J+1)$ in the upper and lower combining states respectively. Alternatively we can describe each vibrational state with the appropriate value of its vibrational quantum number v. In the example below we label the coefficients for the lower state with subscript 0 and for the upper state with subscript 1, appropriate to the fundamental band for which the transition in absorption is from a vibrational state with $v = 0$ to another vibrational state with $v = 1$. Thus to third order $R(J)$ is

```
> N := [B[1],-D[1],H[1]],  [B[0],-D[0],H[0]]:
> R( J, N );
```

$$B_1\,(\,J+1\,)\,(\,J+2\,)-D_1\,(\,J+1\,)^2\,(\,J+2\,)^2 + H_1\,(\,J+1\,)^3\,(\,J+2\,)^3-B_0\,J\,(\,J+1\,) + D_0\,J^2\,(\,J+1\,)^2-H_0\,J^3\,(\,J+1\,)^3$$

To evaluate the parameters of each vibrational state separately we take what are called combination differences between $R(J)$ and $P(J)$. For the parameters of the upper state the appropriate combination is

```
> R( J, N )  - P(J, N );
```

$$B_1\,(\,J+1\,)\,(\,J+2\,)-D_1\,(\,J+1\,)^2\,(\,J+2\,)^2 + H_1\,(\,J+1\,)^3\,(\,J+2\,)^3-B_1\,(\,J-1\,)\,J + D_1\,(\,J-1\,)^2\,J^2-H_1\,(\,J-1\,)^3\,J^3$$

This result is elegantly expressed as a power series in $J+1/2$.

```
> taylor( ", J=-1/2, 10 );
```

$$\left(4\,B_1+\frac{27}{4}\,H_1-6\,D_1\right)\left(J+\frac{1}{2}\right)+(34\,H_1-8\,D_1)\left(J+\frac{1}{2}\right)^3+12\,H_1\left(J+\frac{1}{2}\right)^5$$

Similarly for the combination difference to evaluate the parameters for the lower state,

```
> R( J-1, N )  - P( J+1, N );
```

$$-B_0\,(\,J-1\,)\,J+D_0\,(\,J-1\,)^2\,J^2-H_0\,(\,J-1\,)^3\,J^3 + B_0\,(\,J+1\,)\,(\,J+2\,)-D_0\,(\,J+1\,)^2\,(\,J+2\,)^2 + H_0\,(\,J+1\,)^3\,(\,J+2\,)^3$$

```
> taylor(",J=-1/2, 10);
```

$$\left(4\,B_0+\frac{27}{4}\,H_0-6\,D_0\right)\left(J+\frac{1}{2}\right)+(34\,H_0-8\,D_0)\left(J+\frac{1}{2}\right)^3+12\,H_0\left(J+\frac{1}{2}\right)^5$$

The other principal characteristic of a vibration-rotational band is the band origin. To evaluate this we must explicitly include the vibrational energy $G(v)$. (Previously, when our interest was primarily a combination difference, the vibrational energy must clearly cancel.) The vibration-rotational energy $EvJ(J, v)$ is the sum of the vibrational energy $G(v)$ and the rotational energy $F(J)$. We show an example below to second order, and then redefine the R and P branches accordingly.

```
> EvJ  := (J,v,C)  -> G(v)  + F(J,C):
```

```
> EvJ( J, v, [B[v],-D[v]] );
```

$$\mathrm{G}(v) + B_v\, J\,(J+1) - D_v\, J^2\,(J+1)^2$$

```
> R  := (J,CU,CL)  ->
>    EvJ( J+1, 1, CU ) - EvJ( J, 0, CL ):
```

```
> P  := (J,CU,CL)  ->
>    EvJ( J-1, 1, CU ) - EvJ( J, 0, CL ):
```

The appropriate relation to evaluate the band origin is the following combination sum, which is most meaningfully expressed as a series in J; it contains J to only even powers.

```
> N := [B[1],-D[1]], [B[0],-D[0]]:
> R(J-1,N) + P(J,N);
```

$$\begin{aligned}&2\,\mathrm{G}(1) + B_1\, J\,(J+1) - D_1\, J^2\,(J+1)^2\\&\quad - 2\,\mathrm{G}(0) - B_0\,(J-1)\,J + D_0\,(J-1)^2\,J^2\\&\quad + B_1\,(J-1)\,J - D_1\,(J-1)^2\,J^2\\&\quad - B_0\,J\,(J+1) + D_0\,J^2\,(J+1)^2\end{aligned}$$

```
> collect(",J);
```

$$\begin{aligned}&(-2\,D_1 + 2\,D_0)\;J^4\\&\quad + (-2\,B_0 + 2\,B_1 - 2\,D_1 + 2\,D_0)\;J^2\\&\quad + 2\,\mathrm{G}(1) - 2\,\mathrm{G}(0)\end{aligned}$$

Here $G(1)-G(0)$ as the difference of the vibrational energies specifies the band origin (or band centre).

Just as for the pure rotational band, the vibration-rotational band has a head to which the lines converge. We test first whether the R branch has a head.

For this purpose we need only the first term in $R(J)$

```
> R( J, [B[1]], [B[0]] );
```

$$\begin{aligned}&\mathrm{G}(1) + B_1\,(J+1)\,(J+2) - \mathrm{G}(0)\\&\quad - B_0\,J\,(J+1)\end{aligned}$$

```
> diff(",J);
```

$$B_1\,(J+2) + B_1\,(J+1) - B_0\,(J+1) - B_0\,J$$

```
> Rhead := simplify(solve(", J));
```

$$\mathit{Rhead} := -\frac{1}{2}\,\frac{B_0 - 3\,B_1}{B_0 - B_1}$$

Note that this value is an approximation to the particular value of J at the band head because for any actual line J is an integer.

Likewise we can test for a band head in the P branch.

```
> P(J,[B[1]],[B[0]]);
```

$$\mathrm{G}(1) + B_1\,(J-1)\,J - \mathrm{G}(0) - B_0\,J\,(J+1)$$

```
> diff(",J);
```

$$B_1\,J + B_1\,(J-1) - B_0\,(J+1) - B_0\,J$$

```
> Phead := simplify(solve(",J));
```

$$\mathit{Phead} := -\frac{1}{2}\,\frac{B_1 + B_0}{B_0 - B_1}$$

The value of J at the head of the R branch is a positive number because $B_0 > B_1$ and $B_0 < 3B_1$, whereas the result for the P branch is negative and therefore carries no physical meaning.

The Rotating Vibrator According to Dunham

In 1932 Dunham [1] published an important paper in which he presented a systematic treatment of vibration-rotational energies and related the spectral parameters to structural parameters. The latter describe how the internuclear potential energy varies with the distance between the nuclei; the distance at the minimum energy is called the equilibrium internuclear separation R_e.

Instead of such unsystematic parameters as B, D, H etc., Dunham used an expansion in the form of a double power series in $v + 1/2$ for the vibrational energies and in $J(J+1)$ for the rotational energies in which v and J denote the vibrational and rotational quantum numbers respectively, and $Y_{k,l}$ denote the coefficients. The Maple procedure below computes a truncated power series for this purpose. We show the formal sum and a particular example.

```
> EvJ   := proc(Y,m,n) local k,l;
> sum( sum( Y[k,l]*(v+1/2)^k*(J*(J+1))^l,
>       l=0..n ), k=0..m ) end:
```

```
> EvJ(Y,m,n);
```

$$\sum_{k=0}^{m}\left(\sum_{l=0}^{n} Y_{k,l}\,\left(v+\frac{1}{2}\right)^{k}\,(J\,(J+1))^{l}\right)$$

```
> Ev0 := EvJ(Y, 1, 1 );
```

$$\begin{aligned}\mathit{Ev0} &:= Y_{0,0} + Y_{0,1}\,J\,(J+1) + Y_{1,0}\,\left(v+\frac{1}{2}\right)\\&\quad + Y_{1,1}\,\left(v+\frac{1}{2}\right)\,J\,(J+1)\end{aligned}$$

The function $V(x)$ for potential energy employs the reduced separation variable x defined in terms of instantaneous R and equilibrium R_e internuclear distances

$$x = \frac{R - R_e}{R_e}.$$

Dunham used $V(x)$ in the following form:

```
> V := proc(x,a,n) local j;
> a[0]*x^2*(1+sum(a[j]*x^j,j=1..n)) end:
> V(x,a,4);
```

$$a_0\,x^2\left(1 + a_1\,x + a_2\,x^2 + a_3\,x^3 + a_4\,x^4\right)$$

The method according to which Dunham found the required relations is known as the JBKW procedure [4] after its authors Jeffreys, Brillouin, Kramers and Wentzel. To obtain discrete energies for bound vibrational and rotational states we apply a condition for quantisation, based on the action integral of Bohr and Sommerfeld, that takes the form

$$\oint \sqrt{E_v - V(x)}\,\mathrm{d}x \;+\; ... \;=\; 2\pi B_e^{1/2}(v + 1/2) \quad (1)$$

in which ... indicates integrals of higher order. We solve first the pure vibrational case; hence J is taken as zero. We evaluate the above integral for purposes of illustration [5]: further integrals follow the same pattern. The differential dx is expressed as $\mathrm{d}V(x)/V_1$ in which V_1 is the derivative of $V(x)$. We set the Maple global variable Order to 5 so that series operations are truncated at $O(x^5)$.

```
> Order := 5:
> Vs := series( V(x,a,4), x );
```

$$Vs := a_0\,x^2 + a_0\,a_1\,x^3 + a_0\,a_2\,x^4 + \mathrm{O}(\,x^5\,)$$

We solve[1] for x as a function of $V(x)$ by reverting the above series.

```
> sol := x = solve(V=Vs,x);
```

$$sol := x = \sqrt{\frac{1}{a_0}}\sqrt{V} - \frac{1}{2}\frac{a_1 V}{a_0} + \frac{1}{8}\frac{\left(-4\,a_2 + 5a_1{}^2\right)V^{3/2}}{a_0{}^2\sqrt{\frac{1}{a_0}}}$$
$$+\,\mathrm{O}(\,V^2\,)$$

We generate V_1 and then substitute the above result for x in V_1. Because Maple does not know that a_0 is positive the square roots in the result need to be simplified.

```
> V1 := diff( Vs, x );
```

$$V1 := 2\,a_0\,x + 3\,a_0\,a_1\,x^2 + 4\,a_0\,a_2\,x^3 + \mathrm{O}(\,x^4\,)$$

```
> V1ofV := series( subs( sol, V1 ), V );
```

$$V1ofV := 2\,a_0\sqrt{\frac{1}{a_0}}\sqrt{V} + 2\,a_1\,V +$$
$$\left(\frac{1}{4}\frac{-4\,a_2 + 5\,a_1{}^2}{a_0\sqrt{\frac{1}{a_0}}} - 3\,a_1{}^2\sqrt{\frac{1}{a_0}} + 4\,a_2\sqrt{\frac{1}{a_0}}\right)V^{3/2}$$
$$+\,\mathrm{O}(\,V^2\,)$$

```
> V1ofV := map( simplify,V1ofV,symbolic );
```

$$\begin{aligned}V1ofV := {}& 2\sqrt{a_0}\sqrt{V} + 2\,a_1\,V\\ & - \frac{1}{4}\frac{\left(-12\,a_2 + 7\,a_1{}^2\right)V^{3/2}}{\sqrt{a_0}} + \mathrm{O}(\,V^2\,)\end{aligned}$$

We see that the coefficients of V in this series are simply the potential-energy coefficients a_j. Because we have $\mathrm{d}V(x)/V_1$ we calculate the reciprocal of V_1 and simplify.

```
> V1toM1 := series( 1/V1ofV, V ):
> V1toM1 := map(simplify,V1toM1,symbolic);
```

$$\begin{aligned}V1toM1 := {}& \frac{1}{2}\frac{1}{\sqrt{a_0}\sqrt{V}} - \frac{1}{2}\frac{a_1}{a_0}\\ & + \frac{3}{16}\frac{\left(-4\,a_2 + 5\,a_1{}^2\right)\sqrt{V}}{a_0{}^{3/2}} + \mathrm{O}(\,V\,)\end{aligned}$$

The integrand in the action integral is rewritten in the following form.

$$\sqrt{E_v - \mathrm{V}(\,x\,)} = \sqrt{-\mathrm{V}(\,x\,)}\sqrt{1 - \frac{E_v}{\mathrm{V}(\,x\,)}}$$

We expand the right side as a series in E_v/V using a dummy variable X, and we discard the order term.

```
> series( sqrt( 1-X), X );
```

$$1 - \frac{1}{2}X - \frac{1}{8}X^2 - \frac{1}{16}X^3 - \frac{5}{128}X^4 + \mathrm{O}(\,X^5\,)$$

```
> Epart := subs(X=Ev/V, convert(",polynom));
```

$$Epart := 1 - \frac{1}{2}\frac{Ev}{V} - \frac{1}{8}\frac{Ev^2}{V^2} - \frac{1}{16}\frac{Ev^3}{V^3} - \frac{5}{128}\frac{Ev^4}{V^4}$$

Finally we evaluate the integral, relying on the fact that only terms containing $V(x)^{-1}$ have a residue: each pole contributes $4\pi i$ to the integral.

```
> eval(subs(O=0,Epart * V1toM1 * sqrt(-V)));
```

$$\left(1 - \frac{1}{2}\frac{Ev}{V} - \frac{1}{8}\frac{Ev^2}{V^2} - \frac{1}{16}\frac{Ev^3}{V^3} - \frac{5}{128}\frac{Ev^4}{V^4}\right)$$
$$\left(\frac{1}{2}\frac{1}{\sqrt{a_0}\sqrt{V}} - \frac{1}{2}\frac{a_1}{a_0} + \frac{3}{16}\frac{\left(-4\,a_2 + 5\,a_1{}^2\right)\sqrt{V}}{a_0{}^{3/2}}\right)$$
$$\sqrt{-V}$$

---

[1] The `solve` command in Release 3 returns one solution in the following. In Release 4 it correctly returns two solutions. Users should select the positive solution if using Release 4 or later versions of Maple.

```
> coeff(series(",V,2),V,-1);
```

$$I\left(-\frac{3}{128}\,\frac{Ev^2\left(-4\,a_2+5\,a_1{}^2\right)}{a_0{}^{3/2}}-\frac{1}{4}\,\frac{Ev}{\sqrt{a_0}}\right)$$

The above `coeff` command does not work in Release 4. Users should select the coefficient of V^{-1} in a different way.

```
> integral  := 4*Pi*I*";
```

$$integral := \\ -4\,\pi\left(-\frac{3}{128}\,\frac{Ev^2\left(-4\,a_2+5\,a_1{}^2\right)}{a_0{}^{3/2}}-\frac{1}{4}\,\frac{Ev}{\sqrt{a_0}}\right)$$

We equate the integral with the right side of equation (1) and prepare to obtain E_v as a function of $v+1/2$ to various powers.

```
> eqn := integral = 2*Pi*sqrt(B)*(v+1/2);
```

$$eqn := -4\pi\left(-\frac{3}{128}\,\frac{Ev^2\left(-4a_2+5\,a_1^2\right)}{a_0{}^{3/2}}-\frac{1}{4}\,\frac{Ev}{\sqrt{a_0}}\right)= \\ 2\,\pi\sqrt{B}\left(v+\frac{1}{2}\right)$$

Solving for v first we have

```
> eqn := v = solve( eqn, v );
```

$$eqn := v = \frac{1}{2}\Bigg(\\ -\frac{3}{8}\,\frac{\pi\,Ev^2\,a_2}{a_0{}^{3/2}}+\frac{15}{32}\,\frac{\pi\,Ev^2\,a_1{}^2}{a_0{}^{3/2}}+\frac{\pi\,Ev}{\sqrt{a_0}}-\pi\sqrt{B}\Bigg) \\ \Big/\left(\pi\sqrt{B}\right)$$

We proceed by reverting the equation to find E_v as a series in v

```
> series(rhs(eqn)+O(Ev^3),Ev);
```

$$-\frac{1}{2}+\frac{1}{2}\,\frac{1}{\sqrt{a_0}\,\sqrt{B}}\,Ev+\frac{1}{2}\,\frac{-\frac{3}{8}\,\frac{\pi\,a_2}{a_0{}^{3/2}}+\frac{15}{32}\,\frac{\pi\,a_1{}^2}{a_0{}^{3/2}}}{\pi\sqrt{B}}\,Ev^2+ \\ \mathrm{O}(Ev^3)$$

```
> Ev := solve(v=", Ev);
```

$$Ev := 2\sqrt{a_0}\sqrt{B}\left(v+\frac{1}{2}\right)-\frac{3}{8}\left(-4\,a_2+5\,a_1{}^2\right)B \\ \left(v+\frac{1}{2}\right)^2+\mathrm{O}\left(\left(v+\frac{1}{2}\right)^3\right)$$

To simplify the coefficients we define $\omega = 2\sqrt{a_0B}$

```
> Ev := subs( a[0]=omega^2/4/B, Ev ):
> Ev := simplify( Ev, symbolic );
```

$$Ev := \omega\left(v+\frac{1}{2}\right)-\frac{3}{8}\left(-4\,a_2+5\,a_1{}^2\right)B\left(v+\frac{1}{2}\right)^2 \\ +\mathrm{O}\left(\left(v+\frac{1}{2}\right)^3\right)$$

By comparison of this result with E_{vJ} below

```
> EvJ( Y, 2, 1 );
```

$$Y_{0,0}+Y_{0,1}\,J\,(\,J+1\,)+Y_{1,0}\left(v+\frac{1}{2}\right) \\ +Y_{1,1}\left(v+\frac{1}{2}\right)J\,(\,J+1\,)+Y_{2,0}\left(v+\frac{1}{2}\right)^2 \\ +Y_{2,1}\left(v+\frac{1}{2}\right)^2 J\,(\,J+1\,)$$

we identify $Y_{1,0}$ with ω and $Y_{2,0}$ with

```
> coeff( Ev, v+1/2, 2 );
```

$$-\frac{3}{8}\left(-4\,a_2+5\,a_1{}^2\right)B$$

This calculation can be extended to higher orders by simply increasing the order to which the computations are computed. Note that one must increase the order of $V(x)$ by two units for each extra $Y_{k,0}$. Computationally, the calculations to revert the series are the most expensive.

We proceed to obtain the rotational dependence of the vibrational energies. For this purpose we denote $J(J+1)$ by β, introduce $\gamma = \sqrt{B/a_0} = 2B/\omega$, and add the centrifugal term $\frac{\beta B}{1+x^2}$. Thereby we form the effective potential energy $V(x,\beta)$ that is defined with the following Maple procedure.

```
> V  := proc(x,a,n,beta) local j;
> B*( (x/gamma)^2*
> (1+sum(a[j]*x^j,j=1..n))+beta/(1+x)^2)
> end:
```

We expand $V(x,\beta)/B$ as a truncated power series in x.

```
> series( V(x,a,2,beta)/B, x, 4 );
```

$$\beta-2\,\beta\,x+\left(3\,\beta+\frac{1}{\gamma^2}\right)x^2+\left(-4\,\beta+\frac{a_1}{\gamma^2}\right)x^3+\mathrm{O}(\,x^4\,)$$

Because Dunham's function for potential energy begins at the quadratic term we eliminate the linear term above with a coordinate transformation. We let

$$x_\beta = x-\epsilon(\beta)$$

and expand as a series about $-\epsilon(\beta)$.

```
> series( V(x+epsilon(beta),a,3,beta)/B,
>           x=-epsilon(beta), 5 );
```

$$\beta - 2\beta(x+\varepsilon(\beta)) + \left(3\beta+\frac{1}{\gamma^2}\right)(x+\varepsilon(\beta))^2 + \left(-4\beta+\frac{a_1}{\gamma^2}\right)(x+\varepsilon(\beta))^3 + \left(\frac{a_2}{\gamma^2}+5\beta\right)(x+\varepsilon(\beta))^4 + O\left((x+\varepsilon(\beta))^5\right)$$

We determine $\epsilon(\beta)$ according to the requirement that $\frac{dV(x,\beta)}{dx} = 0$ at $x = \epsilon(\beta)$. The following steps eliminate the linear term and restore the effective potential energy to the rotationless Dunham form plus a constant term.

```
> diff(",x):
> solve("=0,epsilon(beta));
```

$$-x+\gamma^2\beta+\left(-3\gamma^4-\frac{3}{2}a_1\gamma^4\right)\beta^2+\left(-2a_2\gamma^6+\frac{27}{2}a_1\gamma^6+15\gamma^6+\frac{9}{2}{a_1}^2\gamma^6\right)\beta^3+O\left(\beta^4\right)$$

```
> Subs := convert(",polynom):
> series(V(x,a,3,beta)/B,x,5);
```

$$\beta-2\beta x+\left(3\beta+\frac{1}{\gamma^2}\right)x^2+\left(-4\beta+\frac{a_1}{\gamma^2}\right)x^3+\left(\frac{a_2}{\gamma^2}+5\beta\right)x^4+O(x^5)$$

```
> subs( x=Subs, convert(",polynom) ):
> Temp := series(",x,3):
```

The series *Temp* should lack a linear term. We examine its coefficients one at a time expanding them as series in β.

```
> C0 :=
>  simplify(series(coeff(Temp,x,0),beta,5));
```

$$C0 := \beta-\gamma^2\beta^2+\left(3\gamma^4+a_1\gamma^4\right)\beta^3-\frac{1}{4}\gamma^6\left(36a_1+9{a_1}^2+52-4a_2\right)\beta^4+O\left(\beta^5\right)$$

Substituting for γ and simplifying the coefficients we obtain

```
> Y01  := simplify( series(
> B*subs( gamma=2*B/omega, C0 ), beta ) );
```

$$Y01 := B\beta-4\frac{B^3}{\omega^2}\beta^2+16\frac{B^5\left(3+a_1\right)}{\omega^4}\beta^3-16\frac{B^7\left(36a_1+9{a_1}^2+52-4a_2\right)}{\omega^6}\beta^4+O\left(\beta^5\right)$$

The linear coefficient should be zero to a certain order.

```
> C1 :=
> simplify(series(coeff(Temp,x,1),beta,3));
```

$$C1 := O\left(\beta^3\right)$$

The coefficient of the quadratic term is

```
> C2 :=
> simplify(series(coeff(Temp,x,2),beta,3));
```

$$C2 := \frac{1}{\gamma^2}+\left(3+3a_1\right)\beta-\frac{3}{2}\gamma^2\left(6a_1+3{a_1}^2+8-4a_2\right)\beta^2+O\left(\beta^3\right)$$

Comparison of this with Dunham's original function for the potential energy shows that this quantity, which we call gb for short, implies the dependence of γ^{-2} on β.

```
> gb := convert(C2,polynom);
```

$$gb := \frac{1}{\gamma^2}+\left(3+3a_1\right)\beta-\frac{3}{2}\gamma^2\left(6a_1+3{a_1}^2+8-4a_2\right)\beta^2$$

As $Y_{1,0} = 2B/\gamma$, we generate $Y_{1,l}$ by substituting for γ the square root of the above.

```
> simplify(series(2*B*sqrt(rhs(gb)),beta,3));
```

$$2\frac{B}{\gamma}+3B\gamma\left(1+a_1\right)\beta-\frac{3}{4}B\gamma^3\left(18a_1+9{a_1}^2+19-8a_2\right)\beta^2+O\left(\beta^3\right)$$

```
> Y11 := subs( gamma=2*B/omega," );
```

$$Y11 := \omega+6\frac{B^2\left(1+a_1\right)}{\omega}\beta-6\frac{B^4\left(18a_1+9{a_1}^2+19-8a_2\right)}{\omega^3}\beta^2+O\left(\beta^3\right)$$

To obtain the dependence of a_1 and a_2 on β we redo these calculations to greater order. We omit the output of most steps below.

```
> series( V(x+epsilon(beta),a,5,beta)/B,
> x=-epsilon(beta), 7 ):
```

```
> diff(",x):
> solve("=0,epsilon(beta)):
```

```
> Subs := convert(",polynom):
> series(V(x,a,5,beta)/B,x,7):
```

```
> subs( x=Subs, convert(",polynom) ):
> Temp := series(",x,7):
```

We proceed to obtain the coefficient of x^3 that corresponds to $a_1(\beta)/\gamma(\beta)^2$ and the coefficient of x^4 that corresponds to $a_2(\beta)/\gamma(\beta)^2$.

```
> C3 :=
> normal(series(coeff(Temp,x,3),beta,3));
```

$$C3 := -\frac{a_1}{\gamma^2}+\left(-4a_2+4\right)\beta+2\gamma^2\left(-5a_3+6a_2+3a_2a_1-10\right)\beta^2+O\left(\beta^3\right)$$

```
> a1ofbeta :=
> normal(series( C3/gb, beta, 3 );
```

$$a1ofbeta := -a_1 + \left(-4\,a_2 + 4 + 3\,a_1 + 3\,{a_1}^2\right)\gamma^2\,\beta - \frac{1}{2}\gamma^4\left(20\,a_3 - 48\,a_2 - 48\,a_2\,a_1 + 64 + 54\,{a_1}^2 + 27\,{a_1}^3 + 66\,a_1\right)\beta^2 + \mathrm{O}\left(\beta^3\right)$$

```
> C4 :=
> normal(series(coeff(Temp,x,4),beta,3));
```

$$C4 := \frac{a_2}{\gamma^2} + \left(5 + 5\,a_3\right)\beta - \frac{15}{2}\gamma^2\left(2\,a_3 + a_3\,a_1 + 4 - 2\,a_4\right)\beta^2 + \mathrm{O}\left(\beta^3\right)$$

```
> a2ofbeta :=
> factor( series(C4/gb, beta, 3) );
```

$$a2ofbeta := a_2 - \left(-5 - 5\,a_3 + 3\,a_2 + 3\,a_2\,a_1\right)\gamma^2\,\beta + \frac{3}{2}\gamma^4\left(-20\,a_3 - 15\,a_3\,a_1 - 30 + 10\,a_4 + 18\,a_2\,a_1 + 9\,a_2\,{a_1}^2 + 14\,a_2 - 4\,{a_2}^2 - 10\,a_1\right)\beta^2 + \mathrm{O}\left(\beta^3\right)$$

Finally we substitute these β-dependent a_j into $Y_{2,0}$, from the previous stage of the calculations, to obtain $Y_{2,l}$.

```
> Y20 := 3/8*(4*a[2]-5*a[1]^2)*B;
```

$$Y20 := \frac{3}{8}\left(4\,a_2 - 5\,{a_1}^2\right)B$$

```
> subs({a[1]=a1ofbeta, a[2]=a2ofbeta}, Y20):
> Y21 := subs( gamma=2*B/omega,
>           simplify(series(",beta,2)) );
```

$$Y2l := -\frac{3}{8}\left(5\,{a_1}^2 - 4\,a_2\right)B + 3B^3\left(15\,{a_1}^3 + 15\,{a_1}^2 - 26\,a_1\,a_2 + 20\,a_1 - 6\,a_2 + 10\,a_3 + 10\right)\Big/\omega^2\beta + \mathrm{O}\left(\beta^2\right)$$

To obtain $Y_{k,l}$ for $k > 2$, we substitute simultaneously $\gamma(\beta)$ and $a_j(\beta)$ into $Y_{k,0}$. For this purpose we compute to still greater order the series that we have called Temp. We have done it without difficulty up to $Y_{4,l}$. The result obtained for $Y_{3,l}$ up to a_5 follows.

```
> Y31 :=
> series((-1/64*B^2/omega*(-320*
> a[4]+1120*a[3]*a[1]+272*a[2]^2-
> 1800*a[2]*a[1]^2+705*a[1]^4))+
> (5/32*B^4/omega^3*(3600*a[1]^2+
> 2688*a[1]-1088*a[2]+1792*a[3]-
> 576*a[4]+4512*a[1]^3+896*a[5]+
> 816*a[2]^2+3807*a[1]^4+3807*a[1]^5+
> 896-3264*a[4]*a[1]+6576*a[1]*a[2]^2-
> 7560*a[2]*a[1]^2-12072*a[2]*a[1]^3+
> 6960*a[3]*a[1]^2-2880*a[3]*a[2]+
> 3360*a[3]*a[1]-5760*a[1]*a[2]))*
> beta+O(1)*beta^2,beta,2);
```

$$Y3l := -\frac{1}{64}B^2\left(705\,{a_1}^4 - 1800\,{a_1}^2\,a_2 + 1120\,a_1\,a_3 + 272\,{a_2}^2 - 320\,a_4\right)/\omega + \frac{5}{32}B^4\left(3807\,{a_1}^5 + 3807\,{a_1}^4 - 12072\,{a_1}^3\,a_2 + 4512\,{a_1}^3 - 7560\,{a_1}^2\,a_2 + 6960\,{a_1}^2\,a_3 + 6576\,a_1\,{a_2}^2 + 3600\,{a_1}^2 - 5760\,a_1\,a_2 + 3360\,a_1\,a_3 - 3264\,a_1\,a_4 + 816\,{a_2}^2 - 2880\,a_2\,a_3 + 2688\,a_1 - 1088\,a_2 + 1792\,a_3 - 576\,a_4 + 896\,a_5 + 896\right)\Big/\omega^3\beta + \mathrm{O}\left(\beta^2\right)$$

The application of these coefficients $Y_{k,l}$ in fitting frequencies of spectral lines in order to derive values of R_e (from $B = h/(8\pi^2 c\mu R_e^2)$, with μ the reduced mass of the diatomic molecule; h is Planck's constant and c is the velocity of light) involves coding of these expressions and their derivatives with respect to the parameters a_j, ω and B. Maple's generation of Fortran code facilitates the translation of these results into a form suitable for use with other software. Below we show how easily one may generate code fragments for $Y_{1,2}$ and its derivatives.

```
> Y[1,2] := coeff( Y11, beta, 2 );
```

$$Y_{1,2} := -6\,\frac{B^4\left(18\,a_1 + 9\,{a_1}^2 + 19 - 8\,a_2\right)}{\omega^3}$$

```
> fortran(Y[1,2]);

t0 = -6*B**4/omega**3*(18*a(1)+9*a(1)**2+
        19-8*a(2))
```

We compute symbolically the gradient of $Y_{1,2}$ with respect to the four parameters B, ω, a_1, a_2.

```
> G :=
> linalg[grad](Y[1,2],[B,omega,a[1],a[2]]);
```

$$G := \left[-24\,\frac{B^3\left(18\,a_1 + 9\,{a_1}^2 + 19 - 8\,a_2\right)}{\omega^3} \quad 18\,\frac{B^4\left(18\,a_1 + 9\,{a_1}^2 + 19 - 8\,a_2\right)}{\omega^4} \quad -6\,\frac{B^4\left(18 + 18\,a_1\right)}{\omega^3} \quad 48\,\frac{B^4}{\omega^3}\right]$$

The facility for optimization provided by Maple's command *fortran* recognises automatically the common subexpressions present in the gradient G, for example the powers of B; Maple uses temporary variables t1, t2, t3 etc. for this purpose.

```
> fortran(G,optimized);

        t1 = B**2
        t3 = omega**2
        t5 = 1/t3/omega
        t7 = a(1)**2
        t8 = 18*a(1)+9*t7+19-8*a(2)
        t10 = t1**2
        t11 = t3**2
        t15 = t10*t5
        G(1) = -24*t1*B*t5*t8
        G(2) = 18*t10/t11*t8
        G(3) = -6*t15*(18+18*a(1))
        G(4) = 48*t15
```

Conclusion

What we have shown in the first section is that calculations necessary to analyze frequency data from molecular spectra can be, to high order, made easily, quickly and without error, after one has assessed the steps needed to make the calculations to low order. An extension to treat Raman spectra, with its selection rules $\Delta J = 0, \pm 2$, is obvious; such a calculation is a commended exercise for a student.

In the second section, we have for the first time enabled students to undertake Dunham's procedure, or something closely related to it, without tedious and protracted manual labour, and concurrently to achieve results that are useful at the present frontier of research in molecular spectroscopy.

The steps of computations presented here were not the original steps that we made: as multiple ways exist to implement these calculations in Maple, we devoted some time to try to find the *best* form to present the results. What is shown here is a *censored* version of calculations for which we have minimized the number of steps by using the best Maple command for each step.

Once we understand how to implement these calculations, it is conceivable that we should write a program to execute them for approximations of greater order. Although we could do this, we contend that it is far more instructive to a student (and also to ourselves) to see the steps undertaken interactively.

The reader may obtain a Maple worksheet corresponding to the Maple commands in this paper from the authors.

References

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Biographies

John Ogilvie is currently a visiting professor at Oregon State University. After an undergraduate degree in chemistry and physics at University of British Columbia and a research fellowship in physical chemistry at Emmanuel College in University of Cambridge, he has been a professor or visiting professor of chemistry or physics in universities and research institutes on six continents. Besides research in molecular structure and molecular spectrometry, he has active interests in science education, including since 1959 the use of computers to assist learning. Among his 170 publications are the first paper to describe explicit applications of symbolic computation in chemistry and many instances of the use of this approach to derive molecular properties from molecular spectra.

Michael Monagan is assistant professor in mathematics and statistics at Simon Fraser University. A developer of the Maple system, he is interested in applications of symbolic computation in the physical sciences and the use of systems such as Maple to prepare numerical codes; he is an author of Maple facilities to generate Fortran and C code. His other research interests include simplification of formulae, polynomial factorization, greatest common divisors, and resultants, and non-linear dynamical systems.