the computer bulletin board

edited by
Russell H. Batt
Kenyon College
Gambier, OH 43022

Computer Algebra in Chemical Education: Illustrations In Molecular Spectroscopy

J. F. Ogilvie
National Tsing Hua University
Hsinchu 30043, Taiwan
and Academia Sinica
Institute of Atomic and Molecular Sciences
P.O. Box 23-166, Taipei 10764, Taiwan

Although an undergraduate student in chemistry may be expected to have facility with computers for numerical operations, including spreadsheets (*1*) and equation solvers, and the ability to program in a language such as Basic, FORTRAN or Pascal, acquaintance with methods and processors for symbolic computation is mostly lacking. The reason is that mere numeric computing is so well established and so apparently generally applicable an activity that computation of the less well known symbolic kind is largely overlooked. The analytic (algebraic) aspects of chemistry are of greatest value in physical chemistry (*2*), and inadequate mathematical skills of chemistry students have in the past appeared to make physical chemistry unnecessarily difficult. Although no software can remedy instantly lack of skills, one can avoid tedious mathematical manual labor by means of computers just as much as arithmetical labor by means of a pocket calculator. Any computational method is likely to lead to wrong or misleading results if the user fails to understand both the purpose and nature of a computation. Methods of teaching calculus and linear algebra have undergone significant revision due to implementation of symbolic computation (*3*). Software available for ubiquitous microcomputers has become sufficiently functional and reliable that computer algebra should be an essential component of the knowledge and skills of any student of chemistry.

Here we illustrate how to use computer algebra to teach molecular spectroscopy, an integral part of compulsory undergraduate courses in physical chemistry. We use the program Derive[1], which operates on common microcomputers using the MS-DOS operating system. Driven by a menu, this processor of contemporary design incorporates many numerical and graphical abilities in addition to the purely algebraic or symbolic operations of primary concern here. Certain technical properties of Derive necessarily permeate the illustrations, but general features of symbolic computation transcend these particular aspects.

Limiting our attention to relatively simple spectral models typical of undergraduate curriculum in physical chemistry, we consider first the rotational motion of a diatomic molecule. We seek an expression for the frequencies of the transitions according to the rotational selection rule $\Delta J = +1$, J being the rotational quantum number. We assume energies of quantum states to be adequately represented in a series with argument $J(J + 1)$ to positive powers; for convenience we denote this compound variable first by some letter x, to be replaced by $J(J + 1)$ in a succeeding step. For reasons connected with special meanings implied by capital letters in Derive, we use lower-case letters in this calculation even though conventional theory employs generally the upper case. By convention, the coefficients of $J(J + 1)$ to successive positive powers are denoted $B, -D, H, L, M$, etc.; a negative sign is imposed on the second term so as to produce positive numerical values of the coefficients in most spectral applications. In Derive we use the command "Author" to input the expression for the energy, for instance in the form

$$1:\ bx - dxx + hxxx + lxxxx + mxxxxx$$

According to character input mode, each letter is assumed to denote a distinct variable, and lack of another operator between variables implies multiplication. The command "Simplify" produces the result

$$2:\ mx^5 + lx^4 + hx^3 - dx^2 + bx$$

In the true two-dimensional format the exponents are raised above the letters m, x, etc. When we undertake the sequence of menu selections "Manage" and "Substitute", we are prompted to input replacement of each quantity in the highlighted line. In this case we substitute only x by $j(j + 1)$ to produce the result

$$3:\ m(j(j+1))^5 + l(j(j+1))^4 + h(j(j+1))^3 + -d(j(j+1))^2 + b(j(j+1))$$

that we identify with the spectral quantity $F(J)$, the rotational energy of a diatomic molecule in a rotational state denoted by J. Simplification or expansion of this expression yields results of only secondary interest. We proceed to generate the expression for the difference of energy, the transition energy according to the Bohr relation, between adjacent rotational states, $F(J + I) - F(J)$. Therefore we use further substitution, selecting "Manage" and "Substitute", of j by j + 1; after simplification we associate with the rotational energy F(J + 1) the result

$$\begin{aligned}5:\ & b(j + 1)(j + 2) - (j + 1)^2(j + 2)^2 + h(j + 1)^3(j + 2)^2 \\ & + (j + 1)^4(j + 2)^4(j^2m + 3jm + 1 + 2m)\end{aligned}$$

The selection of menu item "Build" to operate on expression 5: with operator "-" and the next expression 3: followed by acceptance of "Done" yields a result that the operation "Expand" makes more attractive. Operations in three sets—"Manage Substitute" with k–1 for j, "Factor k Trivial" and "Manage Substitute" with j + 1 for k—produce a meaningful result for F(J + l)-F(J)

$$\begin{aligned}11:\ & 2(j+1)(5m(j+1)^8 + 2(j+1)^6(2l+5m) + (j+1)^4(3h + 4l + m) + \\ & (j+1)^2(h - 2d) + b)\end{aligned}$$

Readily obtained in about a minute resulting from a sequence of simple, obvious operations, this result represents spectral transitions at the frontiers of research measurements, according to the greatest available spectral resolution and precision of frequency measurement. It is generated in about the same period that a student could obtain by hand only the term of least order, $2B(J + 1)$. Although the actual work of interacting with the computer to

---

[1] Soft Warehouse, Inc., 3660 Waialae Avenue, Suite 304, Honolulu, HI 96816-3236, U.S.A. Derive is available in a student version at modest cost. Note that distinct releases of Derive (or other software subject to continual development) have varied capabilities and may produce results of slightly altered appearance.

produce the desired result is less—and far less tedious—than manual calculation, the task requires as great an understanding by the student of the principles of spectroscopy in order to instruct the computer to undertake the appropriate sequences of operations.

As a second example involving use of other operations (and starting afresh on the monitor by removing all previous expressions), we derive the condition for the formation of a band head in the pure rotational band. A band head occurs when the lines in one branch of a band converge to a limit, at a value J_{BH} of the rotational state of lesser energy, and then reverse their direction. For the present purpose it suffices to include only the first two terms in the transition energy (expression 1 1: above) in the input after selecting "Author",

1: $2\ b\ (j + 1) - 4\ d\ (j + 1)^3$

although it is wise to declare all variables to take by default positive values. We proceed with the sequence of instructions "Calculus", "Differentiate"—with respect to j—once, so as to generate, after "Simplifying".

3: 2(b - 6d(j2 +2j + 1))

Invoking "soLve" to find J_{BH}, generates momentarily two results arising from the above quadratic expression involving j,

4: $j = -\sqrt{b}/\sqrt{(6d)} - 1$

5: $j = \sqrt{b}/\sqrt{(6d)} - 1$

Seeing these results, we readily reject the first that implies a clearly unphysical negative value of J. If we include in 1: another term involving H, the processor can still generate all four roots, but closer inspection is needed to distinguish the physically meaningful root.

For applications in vibration–rotational spectroscopy, we distinguish spectral parameters of separate vibrational states, such as rotational coefficients b0 for $v = 0$ and b1 for $v = 1$; for this purpose, we invoke first the "Options" menu to select "Word" instead of "Character" input mode. We can still use implied multiplication, merely inserting a space between the factors. Extensions of above examples include expressions for frequencies of lines P(J) and R(J) in P and R branches respectively, for combination differences R(J) – P(J) and R(J – 1) – P(J + 1) and the combination sum R(J – 1) + P(J), and for the value of J at the head of a vibration-rotational band. These combination relations have great value in the analysis of a spectral band. Chemistry students have long used these relations to determine separately parameters of each vibrational state from a measured infrared absorption spectrum of gaseous HCl or other simple compound, but by symbolic computation they can derive these relations elegantly and painlessly.

Besides a frequency specifying the location of a line or band in the spectrum, each spectral feature has an intensity that depends on populations of combining states responsible for that feature. For the equilibrium population of a rotational state at temperature T the equation

$$N_J = \mathrm{N}_0(2J + 1)\ \mathrm{e}^{-[hBJ(J+1)/kT]}$$

contains the Boltzmann factor that involves the ratio of rotational energy to mean thermal energy. This expression provides an opportunity to exploit differentiation and solving abilities to determine that the maximum population occurs, to a sufficient approximation (in the absence of terms with D, H, etc.), at a state with a value of the rotational quantum number

$$J_{\mathrm{m}} = -\surd[(kT)/(2hB) - 1$$

For these purposes, operations "Author", "Build", "Calculus", "Expand", "Factor", "soLve", "Manage Substitute", and "Simplify" in Derive are primarily useful as demonstrated above. The student can transfer expressions to a printer for a tangible copy, to a file in statements of form acceptable for Basic, FORTRAN or Pascal programs, or for future work with Derive.

Although present capabilities of numeric processors (such as Basic) are distinct from those of symbolic processors like Derive, a trend exists for numeric processors to be developed to include increasingly varied and numerous features, such as matrix operations and graphical abilities; symbolic processors are concurrently being given diverse and powerful features including such numerical operations as arithmetic in arbitrary precision and numerical solution of equations. With Derive one can fit numerical data for rotational transitions of a particular molecule to a polynomial in $J(J + 1)$, such as $2B(J + 1) - 4D(J + 1)^3$, in order to determine coefficients B and D. Convergence of numeric and symbolic processors is foreseen in the near future, as central processing units of accessible computers acquire greater memory and speed so as to accommodate all these features. Then only one such super-processor (or computer language), that at present Maple[2] approaches most closely, will be required for not only almost all conceivable arithmetical (numerical) applications but also mathematical (symbolic) operations that a chemistry student might require. Until that objective is achieved, it is well worth the effort of undergraduate students of chemistry to learn to use not only numeric processors but also symbolic processors, as the latter not only enable avoidance of tedious manual calculations just as much as the former but also extend relatively easily the scope of chemical calculations almost to the limit of one's imagination *(2, 4–7)*.

---

[2] Waterloo Maple Software, 450 Phillip Street, Waterloo Ontario N2L 5J2 Canada. Maple is available in a student version at modest cost.

An Intermolecular Forces Study Using *IBM PSL*

Christine Eckberg, John Zimmer,
James Reeves, and Charles Ward
University of North Carolina at Wilmington
Wilmington, NC 28403

Interactions between molecules on the microscopic scale influence macroscopic properties of substances. General college chemistry textbooks illustrate this by providing graphs of boiling points for a family of substances, such as