

Algebraic vs. Numerical Methods for Diatomic Diatomic Data Analysis:

{Ending the Ogilvie vs. Coxon/Hajigeorgiou Dispute!!}

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Background

Since early days of quantum mechanics, spectroscopists fitted observed transition energies to difference between level energies using the empirical expansion

$$E(v, J) = \sum_{m=0} \sum_{l=0} Y_{l,m} (v + \tfrac{1}{2})^l [J(J+1)]^m \quad (1)$$

In 1932 Dunham showed that for an internuclear potential function expanded in the form

$$V(r) = a_0 (\xi_D)^2 \left\{ 1 + a_1 (\xi_D) + a_2 (\xi_D)^2 + a_3 (\xi_D)^3 \cdots \right\} \quad (2)$$

in which $\xi_D = (r - r_e)/r_e$, the expansion coefficients $Y_{l,m}$ of Eq (1) were explicitly-known functions of the potential energy expansion parameters:

$$Y_{l,m} = Y_{l,m}(\mu, r_e, \{a_j\})$$

However, the complexity of those expressions grows rapidly with coefficient order $(l + m)$, and with few exceptions,¹ they saw limited practical use for the next half century. Then:

- By the 1980's symbolic computer algebra had made it possible to work practically with almost *arbitrarily* complicated functions.
- By the late 1980's Ogilvie was reporting practical fits to data in which the fitting parameters were not sets of freely varying expansion coefficients, but rather sets of $Y_{l,m}$ coefficients constrained to be inter-related by the Dunham expressions.
- By the early 1990's, this led to direct-fit analyses in which the level energies were represented by Eq. (1), but the parameters being varied were the potential function expansion parameters of Eq. (2) [usually expressed using the “Ogilvie-Tipping” variable $\xi_{OT} = 2 \frac{(r - r_e)}{(r + r_e)}$ instead of ξ_D].

¹ Noteworthy exceptions include work by Niay, Bernagen Coquant and Faytm in 1977 [*Can. J. Phys.* **55**, 1929 (1977)] and by Maki and Lovas in the early 1980's [*J. Mol. Spectrosc.* **95**, 80 (1982) and *ibid* **98**, 146 (1983)]

A “*direct-potential-fit*” (DPF) analysis, in which the simulated transition energies are differences between eigenvalues of a chosen analytic potential function, and the fitted quantities are parameters defining that potential, can be performed in two ways.

- the eigenvalues and partial derivatives required for the least-squares fit may be obtained by numerically solving the appropriate effective radial Schrödinger equation, or ...
- if the potential is expressed as a polynomial expansion, they may be obtained from analytic expressions generated from symbolic computer algebra

However, on fitting *exactly the same potential function model* to *exactly the same data set*, these two methods often gave conflicting results!

Dimensionless RMS deviations (\overline{dd}) for fits to/predictions of high resolution MW and IR data.					
molecule	# data	Ogilvie's algebraic fit		Coxon's numerical fit	
		result	numerical test	result	RADIATOM test
NaCl	1210	0.904	16.18	0.918	4.915
GeS	727	0.948	4.80	0.927	4.207
BrCl	883	0.940	9.35	0.939	19.029
LiH	594	1.103	45.0	1.085	182.6
GaH	1094	0.909	283.3	0.869	608.3

This talk shows that *the source of these discrepancies is an undocumented truncation criterion applied in Ogilvie's algebraic data-analysis program, RADIATOM.*

A ***Direct-Potential-Fit (DPF) Data Analysis*** simulates observed transition energies by solving the radial Schrödinger equation for some assumed model potential, and optimizes potential parameters to yield an optimum fit to the data.

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

where $V_{\text{CN}}(r)$ is the “clamped nuclei” Born-Oppenheimer potential function,

$$\begin{aligned}
 \beta(r) &= (m_e/M_A) Q^A(r) + (m_e/M_B) Q^B(r) && \text{the non-adiabatic kinetic energy BOB function} \\
 \alpha(r) &= (m_e/M_A) R^A(r) + (m_e/M_B) R^B(r) && \text{the non-adiabatic centrifugal BOB function} \\
 \Delta V_{\text{ad}}(r) &= (m_e/M_A) S^A(r) + (m_e/M_B) S^B(r) && \text{the “adiabatic” potential energy correction}
 \end{aligned}$$

A more common working version of this equation is

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

The objective of DPF data analysis is to determine the effective radial potential whose calculated eigenvalue differences accurately reproduce all available data:

$$V_{\text{eff}}(r) = V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r) + \beta(r)[E - V_{\text{CN}}(r)] + \frac{\hbar^2}{2\mu r^2}[1 + \alpha(r) - \beta(r)][J(J + 1)]$$

i.e., to determine the four radial functions $V_{\text{CN}}(r)$, $\Delta V_{\text{ad}}(r)$, $\alpha(r)$ and $\beta(r)$.

Express these functions as power series expansions:

$$V_{\text{CN}}(r) = c_0 \xi^2 \left(1 + \sum_{j=1} c_j \xi^j \right) \quad \text{in which} \quad \xi = \xi_{\text{OT}} = \left(\frac{r - r_e}{r + r_e} \right)$$

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

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

$$\alpha(r) = \frac{m_e}{M_B} \sum_{j=0} t_j^A \xi^j + \frac{m_e}{M_B} \sum_{j=0} t_j^B \xi^j$$

Ogilvie's algebraic approach solves the Schrödinger equation *algebraically* to obtain analytic expressions for the level energies and their partial derivatives in terms of expressions for the Dunham $Y_{l,m}$ coefficients, and uses them in a standard least-squares fit to data.

Coxon's numerical approach solves the Schrödinger equation and fits to optimize the potential function parameters using standard *numerical* methods, applying the Hellman-Feynmann theorem to calculate the required partial derivatives $\frac{\partial E_{v,J}}{\partial p_j} = \left\langle \psi_{v,J}(r) \left| \frac{\partial V_{\text{eff}}(r)}{\partial p_j} \right| \psi_{v,J}(r) \right\rangle$

Both approaches fit to determine values of a set of expansion parameters

$$\{p_j\} = \{ \{c_j\}, \{u_j^A\}, \{u_j^B\}, \{s_j^A\}, \{s_j^B\}, \{t_j^A\}, \{t_j^B\} \}$$

and in principle, *the two approaches should be equivalent and equally reliable!*

Source of the Problem

The algebraic method starts with a radial Schrödinger equation in which the potential function is represented by a polynomial expansion; in Ogilvie's formulation:

$$V(r) = c_0 (\xi_{\text{OT}})^2 \left\{ 1 + c_1 (\xi_{\text{OT}}) + c_2 (\xi_{\text{OT}})^2 + c_3 (\xi_{\text{OT}})^3 \cdots \right\} \quad \text{with} \quad \xi_{\text{OT}} = 2 \frac{(r - r_e)}{(r + r_e)}$$

Solving the Schrödinger equation algebraically yields

$$E(v, J) = \sum_{m=0} \sum_{l=0} Y_{l,m} (v + \tfrac{1}{2})^l [J(J+1)]^m$$

with $Y_{l,m} = Y_{l,m}(\mu, r_e, \{c_j\})$. Fitting transition energies to differences between level energies given by this expression yields values of the potential expansion coefficients $\{c_j\}$.

In a key methodology paper [*J. Phys. B (At. Mol. Opt. Phys.)* **27**, 47 (1994)], Ogilvie stated:

“Following Dunham (1932) and the subsequent extension (Herman and Short 1968), we express the vibration-rotational terms in the systematic form of a double summation

$$\tilde{E}_{vJ} = \sum_{k=0} \sum_{l=0} \left(Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} Z_{kl}^{r,a} + Z_{kl}^{r,b} \right) (v + \tfrac{1}{2})^k [J(J+1)]^l \quad (8)$$

in which we take enough terms coefficients to reproduce accurately the experimental data; ...”

However, ***Ogilvie's Radiatom program does not do this!***

For a potential function which only involves potential coefficients c_j for which $j \leq j_{\text{max}}$, he truncates the double sum in his Eq. (8) (above) to *neglects all $Y_{l,m}$ coefficients for which*

$$2l + m - 2 > j_{\text{max}}$$

This “Ogilvie truncation criterion” is the source of the apparent discrepancies between the “algebraic” and “numerical” DPF methods.

Implications of the Ogilvie Truncation Criterion

For various choices of the highest-order non-zero potential expansion coefficient $c_{j_{\max}}$, this table shows the Ogilvie-criterion cutoff points for the sums in the Dunham eigenvalue expansion.

- e.g.,
- if $j_{\max} = 4$, all $Y_{l,m}$ coefficients for (l, m) combinations below the dashed line are ignored
 - if $j_{\max} = 8$, all $Y_{l,m}$ coefficients for (l, m) combinations below the dotted line are ignored

	$m=0$	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}												

A possible rationalization?

“Dunham algebra” shows that a given $Y_{l,m}$ coefficient depends *only* on potential function expansion coefficients c_j for which $j \leq j_{\max} = 2l + m - 2$. All $Y_{l,m}$ coefficients which could depend even partially on c_j terms not explicitly included in the potential, should be ignored.

My response:

If you do that, your Dunham expansion does not accurately represent the energy levels of the potential defined by your non-zero $\{c_j\}$ coefficients!

Does this explain the algebraic vs. numerical discrepancies?

Test: Repeat the algebraic **RADIATOM** fits while forcing the algebra to include $Y_{l,m}$ coefficients beyond the $2l+m-2 \leq j_{\max}$ limit!

		highest-order potential coefft.		highest-order BOB coefficient			$\overline{d\overline{d}}(\text{fit})$	$\overline{d\overline{d}}(\text{test})$
case		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
BrCl	(i)	$c_4 = 4.05(4)$	c_4	$s_0^{\text{Br}} = 1.70(26)$	$t_0^{\text{Br}} = -0.49(10)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$	0.936	9.136
				$s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Cl}} = -0.65(2)$	$s_0^{\text{Cl}}, t_0^{\text{Cl}}$		
	(ii)	$c_4 = 2.23(4)$	c_6	$s_0^{\text{Br}} = 1.68(26)$	$t_0^{\text{Br}} = -0.52(10)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$	0.938	1.642
				$s_0^{\text{Cl}} = 0.85(6)$	$t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Cl}}, t_0^{\text{Cl}}$		
	(iii)	$c_4 = 2.16(4)$	c_8	$s_0^{\text{Br}} = 1.67(26)$	$t_0^{\text{Br}} = -0.52(10)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$	0.939	1.322
				$s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Cl}}, t_0^{\text{Cl}}$		
	(iv)	$c_4 = 2.15(4)$	c_{10}	$s_0^{\text{Br}} = 1.67(26)$	$t_0^{\text{Br}} = -0.52(10)$	$s_0^{\text{Br}}, t_0^{\text{Br}}$	0.940	1.339
				$s_0^{\text{Cl}} = 0.84(6)$	$t_0^{\text{Cl}} = -0.66(2)$	$s_0^{\text{Cl}}, t_0^{\text{Cl}}$		
	(v)	$c_4 = 2.17(4)$	c_{10}	$s_0^{\text{Br}} = 1.73(27)$	$t_0^{\text{Br}} = -0.53(10)$	$s_6^{\text{Br}}, t_6^{\text{Br}}$	0.939	0.939
				$s_0^{\text{Cl}} = 0.86(6)$	$t_0^{\text{Cl}} = -0.66(1)$	$s_6^{\text{Cl}}, t_6^{\text{Cl}}$		

Conclusion:

1. If the Dunham-type power series it uses internally to represent the data are *truly* summed to convergence, the algebraic method yields *the same* results as numerical DPF methods.
2. Because of the “Ogilvie truncation criterion”, the radial functions determined in all reported **RADIATOM**-based algebraic data analyses *are not* the potential energy and Born-Oppenheimer breakdown functions appearing in the radial Schrödinger equation the method starts from, *but merely internal functions* which can reproduce the input data if used in the (proprietary and not publicly available!) **RADIATOM** program.

Dipole Moments from Only Transition Energy Data?

Claims that dipole moments and rotational g-factors may be determined from fits to *only* transition energy data^{2,3} are based on the assumption that the leading expansion coefficients of the centrifugal non-adiabatic Born-Oppenheimer breakdown term $\alpha(r)$ in the radial Hamiltonian (i.e., the coefficients t_0^A and t_0^B may be unambiguously and uniquely determined.

$$-\frac{\hbar^2}{2\mu}[1 + \beta(r)] \frac{d^2 \psi_{v,J}(r)}{dr^2} + [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] \psi_{v,J}(r) + \frac{\hbar^2}{2\mu r^2}[1 + \alpha(r)][J(J+1)] \psi_{v,J}(r) = E \psi_{v,J}(r) \quad (3)$$

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

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

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

However, Watson had shown [*J. Mol. Spectrosc.* **80**, 411 (1980)], that Eq. (3) can be transformed into one involving *two* modified independent BOB function, which indicates that independent t_0^A and t_0^B values *cannot* be determined from fits to transition energies alone!

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

²J.F. Ogilvie, “Electric Polarity $^+\text{BrCl}^-$ and Rotational g Factor from Analysis of Frequencies of Pure Rotational and Vibration-Rotational Spectra”, *J. Chem. Soc. Faraday Trans.* **91**, 377 (1994).

³J.F. Ogilvie, “The Electric Polarity $^+\text{GeS}^-$ from Analysis of Only Frequencies and Wavenumbers of Pure Rotational and Vibration-Rotation Spectra”, *Mol. Phys.* **88**, 1055 (1996).

Numerical fitting with a modified version of Ogilvie's **RADIATOM** program which extends the Dunham sums to convergence showed that fits of equivalent quality could be obtained using alternate parameterizations which *did not involve any* t_0^A or t_0^B coefficients.

case	highest-order potential coefft.		highest-order BOB coefficient			$\overline{dd}(\text{fit})$	$\overline{dd}(\text{test})$
	fitted	algebra	fitted by RADIATOM		algebra		
NaCl (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}	$u_1^{\text{Cl}} = -7.(3) \times 10^4$	—	u_6^{Cl}	0.928	0.923
GeS (v)	$c_4 = -0.206(25)$	c_{10}	$s_0^{\text{Ge}} = 1.51(41)$	$t_0^{\text{Ge}} = -1.42(13)$	$s_6^{\text{Ge}}, t_6^{\text{Ge}}$	0.928	0.928
				$t_0^{\text{S}} = -1.85(8)$	t_6^{S}		
(vi)	$c_4 = -0.204(26)$	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 (v)	$c_4 = 2.17(4)$	c_{10}	$s_0^{\text{Br}} = 1.73(27)$	$t_0^{\text{Br}} = -0.53(10)$	$s_6^{\text{Br}}, t_6^{\text{Br}}$	0.939	0.939
			$s_0^{\text{Cl}} = 0.86(6)$	$t_0^{\text{Cl}} = -0.66(1)$	$s_6^{\text{Cl}}, t_6^{\text{Cl}}$		
(vi)	$c_4 = 2.18(4)$	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

Conclusion:

3. Numerical fits using an extended version of Ogilvie's **RADIATOM** program confirm that fits to transition energies alone *cannot* determine physically significant t_0^A and t_0^B values, and hence *cannot* determine dipole moment functions or rotational g factors.