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NOTES

Least-Squares Equivalence of Different Representations of Rotational Constants

Observed spectroscopic line positions are often fitted to one of several different representations of a given pair of upper- and lower-state molecular Hamiltonians. For example, there are three representations that are commonly used to fit the observed lines ν_i, $i = 1, 2, \ldots, n$, of the P and R branches of a ${}^1\Sigma$–${}^1\Sigma$ band. First, the band origin ν_0 and the upper- and lower-state rotational constants are considered as the unknown adjustable parameters: $\boldsymbol{\beta}^T = (\nu_0, B', D', B'', D'')$, where $\boldsymbol{\beta}^T$ denotes the transpose of the vector $\boldsymbol{\beta}$. The $\boldsymbol{\beta}$ representation is frequently used when the observed line positions are fitted to calculated line positions obtained by diagonalizing upper- and lower-state molecular Hamiltonians (*1*). Second, the unknown adjustable parameters may include the differences between the upper- and lower-state rotational constants and, say, the lower-state constants: $\boldsymbol{\delta}^T = (\nu_0, \Delta B, \Delta D, B'', D'')$, where $\Delta B = B' - B''$ and $\Delta D = D' - D''$. The $\boldsymbol{\delta}$ representation is often used when many bands have a common vibrational level and when determining polyatomic vibration–rotation coupling constants (*2*). Third, the rotational constants may appear only as sums and differences: $\boldsymbol{\mu}^T = (\nu_0, \Sigma B, \Delta B - \Delta D, \Sigma D, \Delta D)$, where $\Sigma B = B' + B''$ and $\Sigma D = D' + D''$. The $\boldsymbol{\mu}$ representation, which can be expressed in terms of the integral running number m, where $m = -J$ for P lines and $m = J + 1$ for R lines (*3*), is commonly used in the reduction of infrared and Raman data. The minimum-variance, linear, unbiased (MVLU) (*4*) estimates $\hat{\boldsymbol{\beta}}$, $\hat{\boldsymbol{\delta}}$, and $\hat{\boldsymbol{\mu}}$ of the parameters in the $\boldsymbol{\beta}$, $\boldsymbol{\delta}$, and $\boldsymbol{\mu}$ representations are obtained by least-squares solution of the appropriate overdetermined equations

$$\boldsymbol{\nu} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon}, \tag{1a}$$

$$\boldsymbol{\nu} = \mathbf{Y}\boldsymbol{\delta} + \boldsymbol{\varepsilon}, \tag{1b}$$

$$\boldsymbol{\nu} = \mathbf{Z}\boldsymbol{\mu} + \boldsymbol{\varepsilon}. \tag{1c}$$

The elements of the least-squares coefficient matrices **X**, **Y**, and **Z** are well known (Table I). The vector $\boldsymbol{\varepsilon}$ contains the unknown measurement errors in $\boldsymbol{\nu}$, which for simplicity are assumed to be random and independent, to have zero mean, and to be from one probability distribution with unknown variance σ^2. The purpose of this Note is to show the least-squares equivalence of these three representations and to examine the propagation of variance and covariance among them.

A key feature of these representations is that the $\boldsymbol{\beta}$, $\boldsymbol{\delta}$, and $\boldsymbol{\mu}$ vectors are related by linear transformations with square transformation matrices. One set of transformations among the representations is

$$\boldsymbol{\delta} = \mathbf{A}\boldsymbol{\beta}, \tag{2a}$$

$$\boldsymbol{\mu} = \mathbf{B}\boldsymbol{\delta}, \tag{2b}$$

$$\boldsymbol{\beta} = \mathbf{C}\boldsymbol{\mu}, \tag{2c}$$

where the elements of the square matrices **A**, **B**, and **C** are given in Table II. (All other transformations can be expressed in terms of these and their inverses.) Furthermore, the coefficient matrices **X**, **Y**, and **Z** (Eq. 1) are related to the transformation matrices **A**, **B**, and **C** (Eq. 2):

$$\mathbf{X} = \mathbf{YA}, \tag{3a}$$

$$\mathbf{Y} = \mathbf{ZB}, \tag{3b}$$

$$\mathbf{Z} = \mathbf{XC}, \tag{3c}$$

TABLE I

β, δ, and μ Representations

(a) $\nu = X\beta + \epsilon$

$$\begin{bmatrix} \text{R lines} \\ \text{P lines} \end{bmatrix} = \begin{bmatrix} 1 & (J+1)(J+2) & -(J+1)^2(J+2)^2 & -J(J+1) & J^2(J+1)^2 \\ 1 & (J-1)J & -(J-1)^2J^2 & -J(J+1) & J^2(J+1)^2 \end{bmatrix} \begin{bmatrix} \nu_0 \\ B' \\ D' \\ B'' \\ D'' \end{bmatrix} + \begin{bmatrix} \epsilon \end{bmatrix}$$

(b) $\nu = Y\delta + \epsilon$

$$\begin{bmatrix} \text{R lines} \\ \text{P lines} \end{bmatrix} = \begin{bmatrix} 1 & (J+1)(J+2) & -(J+1)^2(J+2)^2 & \left[(J+1)(J+2) - J(J+1)\right] & -\left[(J+1)^2(J+2)^2 - J^2(J+1)^2\right] \\ 1 & (J-1)J & -(J-1)^2J^2 & \left[(J-1)J - J(J+1)\right] & -\left[(J-1)^2J^2 - J^2(J+1)^2\right] \end{bmatrix} \begin{bmatrix} \nu_0 \\ \Delta B \\ \Delta D \\ B'' \\ D'' \end{bmatrix} + \begin{bmatrix} \epsilon \end{bmatrix}$$

(c) $\nu = Z\mu + \epsilon$

$$\begin{bmatrix} \text{R lines} \\ \text{P lines} \end{bmatrix} = \begin{bmatrix} 1 & J+1 & (J+1)^2 & -2(J+1)^3 & -(J+1)^4 \\ 1 & -J & J^2 & 2J^3 & -J^4 \end{bmatrix} \begin{bmatrix} \nu_0 \\ \Sigma B \\ \Delta B - \Delta D \\ \Sigma D \\ \Delta D \end{bmatrix} + \begin{bmatrix} \epsilon \end{bmatrix}$$

as can be verified from the matrix elements given in Tables I and II. The least-squares equivalence of the $\boldsymbol{\beta}$, $\boldsymbol{\delta}$, and $\boldsymbol{\mu}$ representations follows directly from Eqs. (1), (2), and (3).

Consider, for example, the equivalence of the $\boldsymbol{\beta}$ and $\boldsymbol{\delta}$ representations. The least-squares solution of Eq. (1a) yields the MVLU estimate $\hat{\boldsymbol{\beta}}$ of the $\boldsymbol{\beta}$ representation (*5*)

$$\hat{\boldsymbol{\beta}} = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\boldsymbol{\nu}, \tag{4}$$

and the estimated variance–covariance (symmetric) matrix containing the standard errors and correlations associated with $\hat{\boldsymbol{\beta}}$ is

$$\hat{\mathbf{V}}_\beta = \hat{\sigma}_\beta^2(\mathbf{X}^T\mathbf{X})^{-1}, \tag{5}$$

where the estimate of the variance of the measurement errors is

$$\hat{\sigma}_\beta^2 = (\boldsymbol{\nu} - \mathbf{X}\hat{\boldsymbol{\beta}})^T(\boldsymbol{\nu} - \mathbf{X}\hat{\boldsymbol{\beta}})/(n - 5). \tag{6}$$

The transformation $\boldsymbol{\delta} = \mathbf{A}\boldsymbol{\beta}$ (Eq. 2a) can be used to transform the MVLU estimates $\hat{\boldsymbol{\beta}}$ into a set of values $\tilde{\boldsymbol{\delta}}$ in the $\boldsymbol{\delta}$ representation:

$$\tilde{\boldsymbol{\delta}} = \mathbf{A}(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\boldsymbol{\nu}. \tag{7}$$

However, $\mathbf{X} = \mathbf{YA}$ (Eq. 3a), with which Eq. (7) becomes

$$\tilde{\boldsymbol{\delta}} = \mathbf{A}(\mathbf{A}^T\mathbf{Y}^T\mathbf{YA})^{-1}\mathbf{A}^T\mathbf{Y}^T\boldsymbol{\nu}. \tag{8}$$

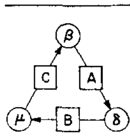
Since the matrices $\mathbf{A}$ and $\mathbf{Y}^T\mathbf{Y}$ are square and have inverses, Eq. (8) simplifies

$$\tilde{\boldsymbol{\delta}} = (\mathbf{Y}^T\mathbf{Y})^{-1}\mathbf{Y}^T\boldsymbol{\nu}. \tag{9}$$

The right-hand side of Eq. (9) is readily identified as the least-squares solution of Eq. (1b); i.e., $\tilde{\boldsymbol{\delta}} = \hat{\boldsymbol{\delta}}$. Thus, the linear transformation $\boldsymbol{\delta} = \mathbf{AB}$ carries the MVLU estimates $\hat{\boldsymbol{\beta}}$ over into the identical set of

TABLE II

Transformations Among the β, δ, and μ Represention



$\delta = A\beta$ $\quad$ $\mu = B\delta$ $\quad$ $\beta = C\mu$

$$A = \begin{bmatrix} 1&0&0&0&0 \\ 0&1&0&-1&0 \\ 0&0&1&0&-1 \\ 0&0&0&1&0 \\ 0&0&0&0&1 \end{bmatrix} \quad B = \begin{bmatrix} 1&0&0&0&0 \\ 0&1&0&2&0 \\ 0&1&-1&0&0 \\ 0&0&1&0&2 \\ 0&0&1&0&0 \end{bmatrix} \quad C = \begin{bmatrix} 1&0&0&0&0 \\ 0&\frac{1}{2}&\frac{1}{2}&0&\frac{1}{2} \\ 0&0&0&\frac{1}{2}&\frac{1}{2} \\ 0&\frac{1}{2}&-\frac{1}{2}&0&-\frac{1}{2} \\ 0&0&0&\frac{1}{2}&-\frac{1}{2} \end{bmatrix}$$

TABLE III

MVLU Estimates for the β, δ, and μ Representations of the (0,0) $E\,^1\Sigma - X\,^1\Sigma$ ThO Band[a]

(a) β representation: $\hat{\sigma}_\beta = 0.00533$, 181 degrees of freedom

$$\hat{\beta} = \begin{bmatrix} \hat{\nu}_0 \\ \hat{B}' \\ \hat{D}' \\ \hat{B}'' \\ \hat{D}'' \end{bmatrix} = \begin{bmatrix} 16320.377 \\ 0.3224994 \\ 1.9971\times10^{-7} \\ 0.3320580 \\ 1.8421\times10^{-7} \end{bmatrix}, \quad \hat{V}_\beta = \begin{bmatrix} 7.2115637\times10^{-7} & & & & \\ 6.5441621\times10^{-10} & 5.6773726\times10^{-11} & & & \\ 3.7329860\times10^{-14} & 3.2685832\times10^{-15} & 2.2016211\times10^{-19} & & \\ 9.1979489\times10^{-10} & 5.7020358\times10^{-11} & 3.2822474\times10^{-15} & 5.7421332\times10^{-11} & \\ 5.6694999\times10^{-14} & 3.2879730\times10^{-15} & 2.2124726\times10^{-19} & 3.3147795\times10^{-15} & 2.2354530\times10^{-19} \end{bmatrix}$$

(b) δ representation: $\hat{\sigma}_\delta = 0.00533$, 181 degrees of freedom

$$\hat{\delta} = \begin{bmatrix} \hat{\nu}_0 \\ \hat{\Delta}B \\ \hat{\Delta}D \\ \hat{B}'' \\ \hat{D}'' \end{bmatrix} = \begin{bmatrix} 16320.377 \\ -0.0095586 \\ 1.550\times10^{-8} \\ 0.3320580 \\ 1.8421\times10^{-7} \end{bmatrix}, \quad \hat{V}_\delta = \begin{bmatrix} 7.2115637\times10^{-7} & & & & \\ -2.6537868\times10^{-10} & 1.5434111\times10^{-13} & & & \\ -1.9365139\times10^{-14} & 1.3142332\times10^{-17} & 1.2128946\times10^{-21} & & \\ 9.1979489\times10^{-10} & -4.0097376\times10^{-13} & -3.2532163\times10^{-17} & 5.7421332\times10^{-11} & \\ 5.6694999\times10^{-14} & -2.6806488\times10^{-17} & -2.2980399\times10^{-21} & 3.3147795\times10^{-15} & 2.2354530\times10^{-19} \end{bmatrix}$$

(c) μ representation: $\hat{\sigma}_\mu = 0.00533$, 181 degrees of freedom

$$\hat{\mu} = \begin{bmatrix} \hat{\nu}_0 \\ \hat{\Sigma}B \\ \hat{\Delta}B-\hat{\Delta}D \\ \hat{\Sigma}D \\ \hat{\Delta}D \end{bmatrix} = \begin{bmatrix} 16320.377 \\ 0.6545574 \\ -0.0095586 \\ 3.8392\times10^{-7} \\ 1.550\times10^{-8} \end{bmatrix}, \quad \hat{V}_\mu = \begin{bmatrix} 7.2115637\times10^{-7} & & & & \\ 1.5742111\times10^{-9} & 2.2823577\times10^{-10} & & & \\ -2.6535932\times10^{-10} & -6.4755450\times10^{-13} & 1.5431483\times10^{-13} & & \\ 9.4024859\times10^{-14} & 1.3153583\times10^{-14} & -4.0467261\times10^{-17} & 8.8620193\times10^{-19} & \\ -1.9365139\times10^{-14} & -5.1921995\times10^{-17} & 1.3141119\times10^{-17} & -3.3831853\times10^{-21} & 1.2128946\times10^{-21} \end{bmatrix}$$

[a] All units are reciprocal centimeters. $\hat{V}_\beta$, $\hat{V}_\delta$, and $\hat{V}_\mu$ are square, symmetric matrices and have not been rounded.

values that would result from a least-squares fit of $\mathbf{v}$ directly to the parameters $\boldsymbol{\delta}$. Similarly, one can show that the variance estimated in this second least-squares fit $\hat{\sigma}_\delta^2$ is identical to $\hat{\sigma}_\beta^2$ (Eq. 6) and that the variance–covariance matrix $\hat{\mathbf{V}}_\delta$ is related to $\hat{\mathbf{V}}_\beta$ (Eq. 5) by the propagation relation

$$\hat{\mathbf{V}}_\delta = \mathbf{A}\hat{\mathbf{V}}_\beta\mathbf{A}^T. \tag{10}$$

Thus $\hat{\boldsymbol{\delta}}$ and $\hat{\boldsymbol{\beta}}$ will generally have different variances, covariances, and correlation coefficients.

Generalizing, it is clear that one can obtain the MVLU estimates $\hat{\boldsymbol{\beta}}$, $\hat{\boldsymbol{\delta}}$, and $\hat{\boldsymbol{\mu}}$ and their estimated variances and covariances by making one least-squares fit using any one of the representations and then transforming these results to the other representations using Eq. (2) and the appropriate form of Eq. (10). Since all three representations are equivalent, one is free to select the one most convenient or appropriate for the needs at hand. These conclusions are straightforwardly verified by numerical calculations. As an example, Table III displays the estimated parameters and variance–covariance matrices obtained by fitting the high-quality measurements for the $E^1\Sigma - X^1\Sigma(0, 0)$ band of ThO (*6*) to the three representations. Equations (2) and (10) are fulfilled within round-off.

It is worth noting the role of covariance in the transformation of the estimated molecular parameters, variance, and covariance from one representation to another. For example, Eq. (10) shows that the variance of $\hat{\Delta}B$ in the $\boldsymbol{\delta}$ representation is related to the variances and covariance of B' and B'' in the $\boldsymbol{\beta}$ representation by

$$\hat{V}_\delta(\Delta B) = \hat{V}_\beta(B') - 2\hat{V}_\beta(B', B'') + \hat{V}_\beta(B''). \tag{11}$$

Because of the strong, positive correlation between B' and B'', the elements of $\hat{\mathbf{V}}_\beta$ in Eq. (11) are all positive and of comparable magnitude. Consequently, the variance of ΔB in the example given in Table III is three orders of magnitude smaller than it would be if B' and B'' were independent (uncorrelated.)

In conclusion, we add a few remarks. First, there are representations that are not rigorously equivalent to the three above, but may be nearly so. Plíva and Telfair (*7*) are examining the combination–difference representation in this regard. Second, the assumptions regarding the errors $\boldsymbol{\varepsilon}$ of the observed lines $\mathbf{v}$ are in no way restrictive. The foregoing analysis can be carried through to the same conclusions using the more general correlated least-squares formulation (*8, 9*) should the measurements be considered to be unequally weighted and/or the errors to be correlated. Third, the above conclusions, which were developed for a single band, apply equally well to a group of bands being reduced to molecular constants simultaneously. Lastly, the above considerations have been for *linear* least-squares only. However, it is not difficult to show that the same conclusions apply to nonlinear least-squares, a point which we have verified numerically in the reduction of $^2\Sigma$–$^2\Pi$, $^3\Pi$–$^3\Sigma$, and $^4\Sigma$–$^4\Pi$ bands to molecular constants.

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