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Vibrational Frequencies and Normal Coordinates: Their Relationship to Force Constants and Inertial Coefficients

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Small variations in the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices can be related linearly to variations in the calculated frequencies and normal coordinates through a transformation matrix, $\boldsymbol{J}$. Explicit expressions are given for the elements of $\boldsymbol{J}$ and $\boldsymbol{J}^{-1}$. Isotope effects on normal-coordinate coefficients are also treated.

In the harmonic-oscillator theory of molecular vibrations, the molecular variables (the frequency parameters, $\lambda_a=4\pi^2c^2\nu_a^2$, and the normal-coordinate coefficients, L_{ia}) are determined completely by the parameters of the model (the elements of the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices in Wilson's notation[1]) and vice versa, through the equations:

$$\boldsymbol{G} = \boldsymbol{L}\tilde{\boldsymbol{L}} \tag{1}$$

and

$$\boldsymbol{\Lambda} = \tilde{\boldsymbol{L}}\boldsymbol{F}\boldsymbol{L} \tag{2a}$$

or

$$\boldsymbol{F} = \tilde{\boldsymbol{L}}^{-1}\boldsymbol{\Lambda}\boldsymbol{L}^{-1} \tag{2b}$$

In the general case, in which the molecule has n vibrational degrees of freedom, there are n frequency parameters and n^2 normal-coordinate coefficients, making a total of $n(n+1)$. Since $\boldsymbol{G}$ and $\boldsymbol{F}$ are symmetric, each has $n(n+1)/2$ independent elements— a total of $n(n+1)$. Thus there should be, in general, $n(n+1)$ relationships between the $[\boldsymbol{G}, \boldsymbol{F}]$ and $[\boldsymbol{\Lambda}, \boldsymbol{L}]$ elements present in Eqs. 1 and 2. Although these relationships are nonlinear, small variations in $\boldsymbol{\Lambda}$ and $\boldsymbol{L}$ can be interpreted in terms of small changes in $\boldsymbol{G}$ and $\boldsymbol{F}$ through a linear transformation:

$$[\Delta\boldsymbol{\Lambda},\ \Delta\boldsymbol{L}] = \boldsymbol{J}[\Delta\boldsymbol{G},\ \Delta\boldsymbol{F}]$$

Similarly, small changes in $\boldsymbol{G}$ and $\boldsymbol{F}$ can be related to small changes in $\boldsymbol{\Lambda}$ and $\boldsymbol{L}$ through the reverse transformation:

$$[\Delta\boldsymbol{G},\ \Delta\boldsymbol{F}] = \boldsymbol{J}^{-1}[\Delta\boldsymbol{\Lambda},\ \Delta\boldsymbol{L}]$$

These transformations, $\boldsymbol{J}$ and $\boldsymbol{J}^{-1}$, can be written as square matrices, the elements of which are the partial derivatives $\partial[\boldsymbol{\Lambda}, \boldsymbol{L}]/\partial[\boldsymbol{G}, \boldsymbol{F}]$ and $\partial[\boldsymbol{G}, \boldsymbol{F}]/\partial[\boldsymbol{\Lambda}, \boldsymbol{L}]$ respectively. The purpose of this paper is to present the algebraic form of these two transformations and to show that each is, in fact, the inverse of the other.

Parts of the $\boldsymbol{J}$ matrix are well known, and their utility has been well established.[2,3] However, the $\boldsymbol{J}$ transformation from $\Delta\boldsymbol{G}$ to $\Delta\boldsymbol{L}$ or the $\boldsymbol{J}^{-1}$ transformation have not previously been described and, as far as we know, the existence of the inverse relationship has not been pointed out.

We will follow current practice and cast the problem in the form of the first-order perturbation theory. Consider the small perturbations $\boldsymbol{G}_1$ and $\boldsymbol{F}_1$ such that:

$$\boldsymbol{G} = \boldsymbol{G}_0 + \boldsymbol{G}_1 \tag{3}$$

and

$$\boldsymbol{F} = \boldsymbol{F}_0 + \boldsymbol{F}_1 \tag{4}$$

These will result in corresponding perturbations in $\boldsymbol{\Lambda}$ and $\boldsymbol{L}$:

$$\boldsymbol{\Lambda} = \boldsymbol{\Lambda}_0 + \boldsymbol{\Lambda}_1 \tag{5}$$

$$\boldsymbol{L} = \boldsymbol{L}_0 + \boldsymbol{L}_1 = \boldsymbol{L}_0(\boldsymbol{E} - \boldsymbol{P}) \tag{6}$$

where $\boldsymbol{E}$ is the unit matrix.[3] It then follows that

$$\boldsymbol{L}^{-1} = \boldsymbol{L}_0^{-1} + \boldsymbol{L}_1^{-1} = (\boldsymbol{E} + \boldsymbol{P})\boldsymbol{L}_0^{-1} \tag{7}$$

From Eqs. 1 and 6, neglecting higher order terms;

$$\boldsymbol{G}_0 + \boldsymbol{G}_1 = \boldsymbol{L}_0(\boldsymbol{E} - \boldsymbol{P})(\boldsymbol{E} - \tilde{\boldsymbol{P}})\tilde{\boldsymbol{L}}_0 \tag{8}$$

whence:

$$\boldsymbol{G}_1 = -\boldsymbol{L}_0(\boldsymbol{P} + \tilde{\boldsymbol{P}})\tilde{\boldsymbol{L}}_0 \tag{9}$$

1) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw Hill Book Company, New York (1955).

2) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **76**, 1132 (1955); W. T. King, I. M. Mills and B. L. Crawford, Jr., *J. Chem. Phys.*, **27**, 455 (1957).

3) I. Nakagawa and T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **80**, 128 (1959). The notation in Eqs. 6 and 7 follows theirs.

or, by rearranging:

$$\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1} = -(\boldsymbol{P}+\tilde{\boldsymbol{P}}) \qquad (10)$$

Similarly, from Eqs. 2a and 6:

$$\boldsymbol{\Lambda}_0 + \boldsymbol{\Lambda}_1 = (\tilde{\boldsymbol{L}}_0 - \tilde{\boldsymbol{P}}\tilde{\boldsymbol{L}}_0)(\boldsymbol{F}_0+\boldsymbol{F}_1)(\boldsymbol{L}_0 - \boldsymbol{L}_0\boldsymbol{P}) \qquad (11)$$

whence:

$$\boldsymbol{\Lambda}_1 = \tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0 - (\tilde{\boldsymbol{P}}\boldsymbol{\Lambda}_0 + \boldsymbol{\Lambda}_0\boldsymbol{P}) \qquad (12)$$

or

$$\boldsymbol{F}_1 = \tilde{\boldsymbol{L}}_0^{-1}\boldsymbol{\Lambda}_1\boldsymbol{L}_0^{-1} + \tilde{\boldsymbol{L}}_0^{-1}(\tilde{\boldsymbol{P}}\boldsymbol{\Lambda}_0 + \boldsymbol{\Lambda}_0\boldsymbol{P})\boldsymbol{L}_0^{-1} \qquad (13)$$

As has been suggested by Nakagawa and Shimanouchi,[3] the transformation is more usefully expressed with respect to $\boldsymbol{P}$ rather than to $\boldsymbol{L}$; therefore, the transformations have been redefined accordingly:

$$[\Delta\boldsymbol{\Lambda}, \boldsymbol{P}] = \boldsymbol{J}[\Delta\boldsymbol{G}, \Delta\boldsymbol{F}]$$

and

$$[\Delta\boldsymbol{G}, \Delta\boldsymbol{F}] = \boldsymbol{J}^{-1}[\Delta\boldsymbol{\Lambda}, \boldsymbol{P}]$$

The elements of $\boldsymbol{J}^{-1}$ are then obtained from Eqs. 9 and 13. In designating matrix elements by a double subscript, we follow convention and write the row index first and the column index second. The $i, j, k,\cdots$ indices refer to internal coordinates, while the $a, b, c,\cdots$ indices refer to normal coordinates.

$$\partial G_{ij}/\partial\lambda_a = 0 \qquad (14)$$

$$\partial G_{ij}/\partial P_{ab} = \partial G_{ij}/\partial P_{ba} = -(L_{ia}L_{jb} + L_{ib}L_{ja}) \qquad (15)$$

$$\partial F_{ij}/\partial\lambda_a = L^{-1}_{ai}L^{-1}_{aj} \qquad (16)$$

$$\partial F_{ij}/\partial P_{ab} = \lambda_a(L^{-1}_{ai}L^{-1}_{bj} + L^{-1}_{bi}L^{-1}_{aj}) \qquad (17)$$

$$(\partial F_{ij}/\partial P_{ba})/\lambda_b = (\partial F_{ij}/\partial P_{ab})/\lambda_a \qquad (18)$$

Equations 14—18 complete the elements of $\boldsymbol{J}^{-1}$.

To determine the elements of $\boldsymbol{J}$, we require $\boldsymbol{\Lambda}$ and $\boldsymbol{P}$ to be explicit functions of $\boldsymbol{G}$ and $\boldsymbol{F}$. It is important to recognize that $\boldsymbol{P}$ is, through Eqs. 10 and 12, a function of $\boldsymbol{G}_1$ and $\boldsymbol{F}_1$. From the diagonal elements of Eq. 12:

$$(\boldsymbol{\Lambda}_1)_{aa} = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{aa} - (P_{aa}\Lambda_{aa} + \Lambda_{aa}P_{aa}) \qquad (19)$$

From Eq. 10:

$$(\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1})_{aa} = -2P_{aa} \qquad (20)$$

and, by combining Eqs. 19 and 20:

$$(\Lambda_1)_{aa} = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{aa} + \lambda_a(\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1})_{aa} \qquad (21)$$

from which:

$$\partial\lambda_a/\partial G_{ij} = 2\lambda_a L^{-1}_{ai}L^{-1}_{aj} \qquad (22)$$

$$\partial\lambda_a/\partial G_{ii} = \lambda_a(L^{-1}_{ai})^2 \qquad (23)$$

$$\partial\lambda_a/\partial F_{ij} = 2L_{ia}L_{ja} \qquad (24)$$

and

$$\partial\lambda_a/\partial F_{ii} = (L_{ia})^2 \qquad (25)$$

The expression for P_{ab} as an explicit function of $\boldsymbol{G}$ and $\boldsymbol{F}$ follows from the off-diagonal elements of Eqs. 10 and 12:

$$-(P_{ab} + P_{ba}) = (\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1})_{ab} \qquad (26)$$

and

$$P_{ba}\lambda_b + \lambda_a P_{ab} = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{ab} \qquad (27)$$

By multiplying Eq. 26 by λ_b and by adding Eq. 27:

$$P_{ab}(\lambda_a - \lambda_b) = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{ab} + \lambda_b(\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1})_{ab} \qquad (28)$$

Similarly:

$$P_{ba}(\lambda_b - \lambda_a) = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{ab} + \lambda_a(\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1})_{ab} \qquad (29)$$

From Eqs. 28 and 29:

$$\partial P_{ab}/\partial F_{ij} = -\partial P_{ba}/\partial F_{ij} = (\lambda_a - \lambda_b)^{-1}(L_{ia}L_{jb} + L_{ib}L_{ja}) \qquad (30)$$

$$\partial P_{ab}/\partial F_{ii} = -\partial P_{ba}/\partial F_{ii} = (\lambda_a - \lambda_b)^{-1}L_{ia}L_{ib} \qquad (31)$$

$$\partial P_{ab}/\partial G_{ij} = [\lambda_b/(\lambda_a - \lambda_b)](L^{-1}_{ai}L^{-1}_{bj} + L^{-1}_{aj}L^{-1}_{bi}) \qquad (32)$$

$$\partial P_{ab}/\partial G_{ii} = [\lambda_b/(\lambda_a - \lambda_b)]L^{-1}_{ai}L^{-1}_{bi} \qquad (33)$$

$$(\partial P_{ba}/\partial G_{ij})/\lambda_a = -(\partial P_{ab}/\partial G_{ij})/\lambda_b \qquad (34)$$

$$(\partial P_{ba}/\partial G_{ii})/\lambda_a = -(\partial P_{ab}/\partial G_{ii})/\lambda_b \qquad (35)$$

Finally, from the diagonal elements of Eq. 9:

$$\partial P_{aa}/\partial G_{ij} = -L^{-1}_{ai}L^{-1}_{aj} \qquad (36)$$

and

$$\partial P_{aa}/\partial G_{ii} = -\frac{1}{2}(L^{-1}_{ai})^2 \qquad (37)$$

and from Eq. 20:

$$\partial P_{aa}/\partial F_{ii} = \partial P_{aa}/\partial F_{ij} = 0 \qquad (38)$$

Eqs. 22—25, 30—33, and 36—38 complete the elements of $\boldsymbol{J}$.

The complete transformations, $\boldsymbol{J}$ and $\boldsymbol{J}^{-1}$, for the particular case of $n=2$ are given in Tables I and II. The product matrices, $\boldsymbol{J}\boldsymbol{J}^{-1}$ and $\boldsymbol{J}^{-1}\boldsymbol{J}$, for the general case have also been constructed. As is shown in Tables III and IV, these matrices are indeed equal to the unit matrix [order of $n(n+1)$]. Accordingly, $\boldsymbol{J}^{-1}$ is now confirmed to be both the left and the right inverse of $\boldsymbol{J}$.

Similar transformations relate $[\Delta\boldsymbol{\Lambda}, \Delta\boldsymbol{L}]$ and also $[\Delta\boldsymbol{\Lambda}, \Delta\boldsymbol{L}^{-1}]$ to $[\Delta\boldsymbol{G}, \Delta\boldsymbol{F}]$. From Eqs. 6 and 7.

$$\boldsymbol{P} = \boldsymbol{L}_1^{-1}\boldsymbol{L}_0 = -\boldsymbol{L}_0^{-1}\boldsymbol{L}_1 \qquad (39)$$

whence:

$$\partial P_{ab}/\partial L^{-1}_{ai} = L_{ib} \qquad (40)$$

and

$$\partial P_{ba}/\partial L_{ia} = -L^{-1}_{bi} \qquad (41)$$

TABLE I. THE $\boldsymbol{J}$ MATRIX

	ΔG_{11}	ΔG_{22}	ΔG_{12}	ΔF_{11}	ΔF_{22}	ΔF_{12}
$\Delta\lambda_1$	$\lambda_1(L_{11}^{-1})^2$	$\lambda_1(L_{12}^{-1})^2$	$2\lambda_1 L_{11}^{-1}L_{12}^{-1}$	$L_{11}{}^2$	$L_{21}{}^2$	$2L_{11}L_{21}$
$\Delta\lambda_2$	$\lambda_2(L_{21}^{-1})^2$	$\lambda_2(L_{22}^{-1})^2$	$2\lambda_2 L_{21}^{-1}L_{22}^{-1}$	$L_{12}{}^2$	$L_{22}{}^2$	$2L_{12}L_{22}$
ΔP_{11}	$-\frac{1}{2}(L_{11}^{-1})^2$	$-\frac{1}{2}(L_{12}^{-1})^2$	$-L_{11}^{-1}L_{12}^{-1}$	0	0	0
ΔP_{22}	$-\frac{1}{2}(L_{21}^{-1})^2$	$-\frac{1}{2}(L_{22}^{-1})^2$	$-L_{21}^{-1}L_{22}^{-1}$	0	0	0
ΔP_{12}	$\frac{\lambda_2}{\lambda_1-\lambda_2}L_{11}^{-1}L_{21}^{-1}$	$\frac{\lambda_2}{\lambda_1-\lambda_2}L_{12}^{-1}L_{22}^{-1}$	$\frac{\lambda_2}{\lambda_1-\lambda_2}(L_{11}^{-1}L_{22}^{-1}+L_{12}^{-1}L_{21}^{-1})$	$\frac{1}{\lambda_1-\lambda_2}L_{11}L_{12}$	$\frac{1}{\lambda_1-\lambda_2}L_{21}L_{22}$	$\frac{1}{\lambda_1-\lambda_2}(L_{11}L_{22}+L_{12}L_{21})$
ΔP_{21}	$\frac{\lambda_1}{\lambda_2-\lambda_1}L_{21}^{-1}L_{11}^{-1}$	$\frac{\lambda_1}{\lambda_2-\lambda_1}L_{22}^{-1}L_{12}^{-1}$	$\frac{\lambda_1}{\lambda_2-\lambda_1}(L_{21}^{-1}L_{12}^{-1}+L_{22}^{-1}L_{11}^{-1})$	$\frac{1}{\lambda_2-\lambda_1}L_{12}L_{11}$	$\frac{1}{\lambda_2-\lambda_1}L_{22}L_{21}$	$\frac{1}{\lambda_2-\lambda_1}(L_{12}L_{21}+L_{11}L_{22})$

TABLE II. THE $\boldsymbol{J}^{-1}$ MATRIX

	$\Delta\lambda_1$	$\Delta\lambda_2$	ΔP_{11}	ΔP_{22}	ΔP_{12}	ΔP_{21}
ΔG_{11}	0	0	$-2L_{11}{}^2$	$-2L_{12}{}^2$	$-2L_{11}L_{12}$	$-2L_{12}L_{11}$
ΔG_{22}	0	0	$-2L_{21}{}^2$	$-2L_{22}{}^2$	$-2L_{21}L_{22}$	$-2L_{22}L_{21}$
ΔG_{12}	0	0	$-2L_{11}L_{21}$	$-2L_{12}L_{22}$	$-(L_{11}L_{22}+L_{12}L_{21})$	$-(L_{12}L_{21}+L_{11}L_{22})$
ΔF_{11}	$(L_{11}^{-1})^2$	$(L_{21}^{-1})^2$	$2\lambda_1(L_{11}^{-1})^2$	$2\lambda_2(L_{21}^{-1})^2$	$2\lambda_1 L_{11}^{-1}L_{21}^{-1}$	$2\lambda_2 L_{21}^{-1}L_{11}^{-1}$
ΔF_{22}	$(L_{12}^{-1})^2$	$(L_{22}^{-1})^2$	$2\lambda_1(L_{12}^{-1})^2$	$2\lambda_2(L_{22}^{-1})^2$	$2\lambda_1 L_{12}^{-1}L_{22}^{-1}$	$2\lambda_2 L_{22}^{-1}L_{12}^{-1}$
ΔF_{12}	$L_{11}^{-1}L_{12}^{-1}$	$L_{21}^{-1}L_{22}^{-1}$	$2\lambda_1 L_{11}^{-1}L_{12}^{-1}$	$2\lambda_2 L_{21}^{-1}L_{22}^{-1}$	$\lambda_1(L_{11}^{-1}L_{22}^{-1}+L_{21}^{-1}L_{12}^{-1})$	$\lambda_2(L_{21}^{-1}L_{12}^{-1}+L_{11}^{-1}L_{22}^{-1})$

Table III. The elements of the JJ^{-1} matrix

Row	Column	Elements*
$\Delta\lambda_a$	$\Delta\lambda_c$	$E_{ca}{}^2 \begin{cases}=1 \text{ only if } a=c \\ =0 \text{ otherwise}\end{cases}$
$\Delta\lambda_a$	ΔP_{cd}	$2\lambda_c E_{ca}E_{da} - 2\lambda_a E_{ac}E_{ad} = 0$
ΔP_{aa}	$\Delta\lambda_c$	0
ΔP_{aa}	ΔP_{cd}	$E_{ac}E_{ad} \begin{cases}=1 \text{ only if } a=c=d \\ =0 \text{ otherwise}\end{cases}$
ΔP_{ab} $(a \neq b)$	$\Delta\lambda_c$	$E_{ca}E_{cb}/(\lambda_a-\lambda_b)=0$
ΔP_{ab} $(a \neq b)$	ΔP_{cd}	$[\lambda_c(E_{ca}E_{db}+E_{cb}E_{da}) - \lambda_b(E_{ac}E_{bd}+E_{ad}E_{bc})]/(\lambda_a-\lambda_b)$ $=(E_{ac}E_{bd}+E_{ad}E_{bc})(\lambda_c-\lambda_b)/(\lambda_a-\lambda_b) \begin{cases}=1 \text{ only if } a=c \text{ and } b=d \\ =0 \text{ otherwise}\end{cases}$

* The unit matrix $\boldsymbol{E}$ was derived from the product of $\boldsymbol{L}^{-1}\cdot\boldsymbol{L}$.

Table IV. The elements of the $J^{-1}J$ matrix

Row $(i \leq j)$	Column $(k \leq l)$	Elements*
ΔG_{ij}	ΔG_{kk}	$E_{ik}E_{jk} \begin{cases}=1 \text{ only if } i=j=k \\ =0 \text{ otherwise}\end{cases}$
ΔG_{ij}	ΔG_{kl} $(k \neq 1)$	$E_{ik}E_{jl}+E_{il}E_{jk} \begin{cases}=1 \text{ only if } i=k \text{ and } j=l \\ =0 \text{ otherwise}\end{cases}$
ΔG_{ij}	ΔF_{kl}	0
ΔF_{ij}	ΔG_{kl}	0
ΔF_{ij}	ΔF_{kk}	$E_{ki}E_{kj} \begin{cases}=1 \text{ only if } i=j=k \\ =0 \text{ otherwise}\end{cases}$
ΔF_{ij}	ΔF_{kl} $(k \neq l)$	$E_{ki}E_{lj}+E_{kj}E_{li} \begin{cases}=1 \text{ only if } i=k \text{ and } j=l \\ =0 \text{ otherwise}\end{cases}$

* The unit matrix $\boldsymbol{E}$ was derived from the product of $\boldsymbol{L}\cdot\boldsymbol{L}^{-1}$.

Then:

$$\frac{\partial}{\partial L_{ia}} = \sum_b \frac{\partial P_{ba}}{\partial L_{ia}} \cdot \frac{\partial}{\partial P_{ba}} = \sum_b (-L^{-1}_{b\,i}) \frac{\partial}{\partial P_{ba}} \tag{42}$$

and

$$\frac{\partial}{\partial L^{-1}_{a\,i}} = \sum_b \frac{\partial P_{ab}}{\partial L^{-1}_{a\,i}} \cdot \frac{\partial}{\partial P_{ab}} = \sum_b L_{ib} \frac{\partial}{\partial P_{ab}} \tag{43}$$

Simple expressions may be derived for example, by substituting Eq. 39 into Eq. 9:

$$\boldsymbol{G}_1 = \boldsymbol{L}_0(\boldsymbol{L}_0^{-1}\boldsymbol{L}_1 + \tilde{\boldsymbol{L}}_1\tilde{\boldsymbol{L}}_0^{-1})\tilde{\boldsymbol{L}}_0 = \boldsymbol{L}_1\tilde{\boldsymbol{L}}_0 + \boldsymbol{L}_0\tilde{\boldsymbol{L}}_1 \tag{44}$$

whence:

$$\partial G_{ii}/\partial L_{ia} = 2L_{ia} \tag{45}$$

$$\partial G_{ij}/\partial L_{ja} = L_{ia} \tag{46}$$

$$\partial G_{ij}/\partial L_{ka} = 0 \qquad (k \neq i,\ j) \tag{47}$$

Expressions for the $\boldsymbol{F}$ matrix may be derived by substituting Eq. 39 into Eq. 13:

$$\boldsymbol{F}_1 = \tilde{\boldsymbol{L}}_0^{-1}\boldsymbol{\Lambda}_1\boldsymbol{L}_0^{-1} - \tilde{\boldsymbol{L}}_0^{-1}(\boldsymbol{\Lambda}_0\boldsymbol{L}_0^{-1}\boldsymbol{L}_1 + \tilde{\boldsymbol{L}}_1\tilde{\boldsymbol{L}}_0^{-1}\boldsymbol{\Lambda}_0)\tilde{\boldsymbol{L}}_0^{-1} = \tilde{\boldsymbol{L}}_0^{-1}\boldsymbol{\Lambda}_1\boldsymbol{L}_0^{-1} - (\boldsymbol{F}_0\boldsymbol{L}_1\boldsymbol{L}_0^{-1} + \tilde{\boldsymbol{L}}_0^{-1}\tilde{\boldsymbol{L}}_1\boldsymbol{F}_0) \tag{48}$$

whence:

$$\partial F_{ij}/\partial L_{ka} = -(F_{ik}L^{-1}_{a\,j} + F_{jk}L^{-1}_{a\,i}) \tag{49}$$

We have found the $\boldsymbol{J}$ and $\boldsymbol{J}^{-1}$ transformations to be particularly useful in the propagation of uncertainties in the force constants and geometrical parameter to obtain estimates of the uncertainties in derived quantities; these derived quantities may include, for example, calculated frequencies, normal coordinate coefficients, Coriolis coefficients, and dipole-moment derivatives with respect to internal coordinates. They may also be useful in the more chemical group-frequency problems which are usually handled by perturbation formalism.

Appendix

Isotope Effects on Normal Coordinate Coefficients.—Small variations in atomic masses Δm_t have been previously[4] related with variations in frequency parameters λ_a. The present results may also be used to treat the isotope effects on normal-coordinate coefficients.

The $\boldsymbol{G}$ matrix is given by[1]

$$\boldsymbol{G} = \boldsymbol{B}\boldsymbol{M}^{-1}\tilde{\boldsymbol{B}} \tag{A-1}$$

where $\boldsymbol{M}^{-1}$ is the inverse mass matrix and the matrix $\boldsymbol{B}$ is the transformation from the Cartesian coordinates to the internal coordinates. Consider small variations[5] $\boldsymbol{M}_1$ such that

4) T. Miyazawa, *J. Mol. Spectry.*, **13**, 321 (1964).

5) The requirement is that the relative changes in masses, i. e. the elements of $\boldsymbol{M}_1\boldsymbol{M}_0^{-1}$, are small.

$$\boldsymbol{M} = \boldsymbol{M}_0 + \boldsymbol{M}_1 \tag{A-2}$$

The corresponding perturbation in $\boldsymbol{M}^{-1}$ is

$$\boldsymbol{M}^{-1} = \boldsymbol{M}_0^{-1} + \boldsymbol{M}_1^{-1} \tag{A-3}$$

where

$$\boldsymbol{M}_1^{-1} = -\boldsymbol{M}_0^{-1}\boldsymbol{M}_1\boldsymbol{M}_0^{-1} \tag{A-4}$$

This results in a small perturbation in $\boldsymbol{G}$, given by

$$\boldsymbol{G}_1 = \boldsymbol{B}\boldsymbol{M}_1^{-1}\tilde{\boldsymbol{B}} = -\boldsymbol{B}\boldsymbol{M}_0^{-1}\boldsymbol{M}_1\boldsymbol{M}_0^{-1}\tilde{\boldsymbol{B}} \tag{A-5}$$

whence

$$\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1} = -\boldsymbol{L}_0^{-1}\boldsymbol{B}\boldsymbol{M}_0^{-1}\boldsymbol{M}_1\boldsymbol{M}_0^{-1}\tilde{\boldsymbol{B}}\tilde{\boldsymbol{L}}_0^{-1} \tag{A-6}$$

Since the normal-coordinate coefficients $\boldsymbol{L}^{\mathrm{X}}$ for Cartesian displacement coordinates are given[6] as

$$\boldsymbol{L}^{\mathrm{X}} = \boldsymbol{M}^{-1}\tilde{\boldsymbol{B}}\tilde{\boldsymbol{L}}^{-1} \tag{A-7}$$

it follows that

$$\boldsymbol{L}_0^{-1}\boldsymbol{G}_1\tilde{\boldsymbol{L}}_0^{-1} = -\tilde{\boldsymbol{L}}_0^{\mathrm{X}}\boldsymbol{M}_1\boldsymbol{L}_0^{\mathrm{X}} \tag{A-8}$$

Small corresponding variations in the frequency parameters may be derived by substituting Eq. A-8 into Eq. 19,

$$\Delta\lambda_a = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{aa} - \lambda_a(\tilde{\boldsymbol{L}}_0^{\mathrm{X}}\boldsymbol{M}_1\boldsymbol{L}_0^{\mathrm{X}})_{aa} \tag{A-9}$$

giving, as derived previously,[4]

$$\partial\lambda_a/\partial m_t = -\lambda_a[(L^x_{t\,a})^2 + (L^y_{t\,a})^2 + (L^z_{t\,a})^2] \tag{A-10}$$

where m_t is the mass of the t-th atom.

Similarly, by substituting Eq. A-8 into Eqs. 20 and 28,

$$P_{aa} = \frac{1}{2}(\tilde{\boldsymbol{L}}_0^{\mathrm{X}}\boldsymbol{M}_1\boldsymbol{L}_0^{\mathrm{X}})_{aa} \tag{A-11}$$

and

$$P_{ab}(\lambda_a - \lambda_b) = (\tilde{\boldsymbol{L}}_0\boldsymbol{F}_1\boldsymbol{L}_0)_{ab} - \lambda_b(\tilde{\boldsymbol{L}}_0^{\mathrm{X}}\boldsymbol{M}_1\boldsymbol{L}_0^{\mathrm{X}})_{ab} \tag{A-12}$$

Accordingly,

$$\partial P_{aa}/\partial m_t = \frac{1}{2}[(L^x_{t\,a})^2 + (L^y_{t\,a})^2 + (L^z_{t\,a})^2] \tag{A-13}$$

and

$$\partial P_{ab}/\partial m_t = -[\lambda_b/(\lambda_a - \lambda_b)] \times [L^x_{t\,a}L^x_{t\,b} + L^y_{t\,a}L^y_{t\,b} + L^z_{t\,a}L^z_{t\,b}] \tag{A-14}$$

This $\boldsymbol{P}$ matrix may also be used in expressing small variations in the $\boldsymbol{L}^{\mathrm{X}}$ matrix as shown below,

$$\boldsymbol{L}^{\mathrm{X}} = \boldsymbol{L}_0^{\mathrm{X}} + \boldsymbol{L}_1^{\mathrm{X}} \tag{A-15}$$

where

$$\begin{aligned}\boldsymbol{L}_1^{\mathrm{X}} &= (\boldsymbol{M}_0^{-1} - \boldsymbol{M}_0^{-1}\boldsymbol{M}_1\boldsymbol{M}_0^{-1}) \\ &\quad \times \tilde{\boldsymbol{B}}\tilde{\boldsymbol{L}}_0^{-1}(\boldsymbol{E} + \tilde{\boldsymbol{P}}) - \boldsymbol{L}_0^{\mathrm{X}} \\ &= \boldsymbol{L}_0^{\mathrm{X}}\tilde{\boldsymbol{P}} - \boldsymbol{M}_0^{-1}\boldsymbol{M}_1\boldsymbol{L}_0^{\mathrm{X}}\end{aligned} \tag{A-16}$$

6) B. L. Crawford, Jr., and W. H. Fletcher, *J. Chem. Phys.*, **19**, 141 (1951).