A New Method for Computing Vibrational Force Constants

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Summary Initial tests of the method of Fletcher and Powell suggest that it overcomes all the computational difficulties associated with older methods.

IN order to compute the vibrational force constants of a molecule one seeks a matrix **F** which satisfies the n equations

$$\mathbf{G F L} = \mathbf{L\Lambda} \qquad (1)$$

where **G** is a constant symmetric matrix derived from the molecular structure, **F** is symmetric and $\mathbf{\Lambda} = \text{diag}\ (\lambda_1 \cdots \lambda_n)$. The eigenvalues λ_k are related to the vibration frequencies ν_k, measured by i.r. and Raman spectroscopy, as $\lambda_k = 4\pi^2\nu_k^2$ so that when **F** is in N m^{-1}, ν_k is in cm^{-1} and **G** is in atomic mass units $\lambda_k = (\nu_k/130{\cdot}28)^2$. It is well known that the Gauss–Newton–Raphson (GNR) method of solving equation (1) often fails to converge to a satisfactory solution.[1] The method of Fletcher and Powell[2] (FP) has shown satisfactory convergence properties in all the model calculations attempted and promises generally to supersede the GNR method.

In the FP method, the force constants are iteratively refined so that the calculated eigenvalues λ_k^r agree as closely as possible with the observed values λ_k by minimising a function such as

$$R^r = \sum^k w_k(\lambda_k - \lambda_k^r)^2 \qquad (2)$$

I call this function an R factor by analogy with X-ray crystallography. r is an iteration number, and w_k is a weight associated with the kth residual. The unknown force constants are placed in a vector $\mathbf{f}^r$ from which $\mathbf{F}^r$ may be derived by the **Z** matrix formalism[3] as $F_{ij}^r = \sum^l Z_{(ij)l} f_l^r$. It is assumed that in the region of the minimum

$$R^r = \text{const} + \tilde{\mathbf{g}}^r\mathbf{f}^r + \tfrac{1}{2}\tilde{\mathbf{f}}^r\mathbf{D}^r\mathbf{f}^r \qquad (3)$$

where $\mathbf{g}^r$ is a gradient vector with $g_i^r = (\partial R/\partial f_i)^r$ and $D_{ij}^r = (\partial^2 R/\partial f_i\,\partial f_j)^r$. A positive definite approximation $\mathbf{H}^r$ to $(\mathbf{D}^r)^{-1}$ is used to generate a set of "conjugate directions of search" as a vector $\mathbf{s}^r = -\mathbf{H}^r\mathbf{g}^r$ and the R factor is minimised along each search direction in turn, *i.e.* the quantities α^r are found such that $\mathbf{f}^{r+1} = \mathbf{f}^r + \alpha^r\mathbf{s}^r$ gives a local minimum. $\mathbf{H}^r$ is systematically updated at each iteration and becomes a better approximation to $(\mathbf{D}^r)^{-1}$ until eventually the global minimum in R is found. Thus the method requires initial estimates $\mathbf{f}^1$ and $\mathbf{H}^1$ and that $\mathbf{g}^r$ and R^r can be calculated.

The elements of $\mathbf{g}^r$ are obtained by differentiating equation (2) as

$$g_i^r = -2\sum^k w_k\,\Delta\lambda_k^r\,(\partial\lambda_k/\partial f_i)^r \qquad (4)$$

where $\Delta\lambda_k^r = \lambda_k - \lambda_k^r$. When $\mathbf{L}^r$ is so normalised that $\mathbf{L}^r\tilde{\mathbf{L}}^r = \mathbf{G}$, equation (1) becomes $\tilde{\mathbf{L}}^r\mathbf{F}^r\mathbf{L}^r = \mathbf{\Lambda}^r$ so that by first-order perturbation theory

$$\text{(a)}\ (\partial\lambda_k/\partial F_{ij})^r = (L_{ik}^r)^2;\ \text{(b)}\ (\partial\lambda_k/\partial F_{ij})^r = 2L_{ik}^rL_{jk}^r \qquad (5)$$

The Jacobian of derivatives in equation (4) is therefore given by

$$J_{kl}^r = (\partial\lambda_k/\partial f_l)^r = \sum^{(ij)} (\partial\lambda_k/\partial F_{ij})^r\,Z_{(ij)l} \qquad (6)$$

When R^r is minimised, the gradient is zero and

$$\mathbf{g}^r = -2\tilde{\mathbf{J}}^r\mathbf{W}\,\Delta\boldsymbol{\lambda}^r = \mathbf{O} \qquad (7)$$

where $\mathbf{W} = \text{diag}\ (w_1 \cdots w_n)$. Therefore, either $\Delta\boldsymbol{\lambda}$ is a zero vector and the frequencies are fitted exactly, or $\tilde{\mathbf{J}}^r\mathbf{W}\,\mathbf{J}^r$ is singular at the minimum. The FP method with all $\alpha^r = 1$ would be equivalent to the GNR method if $\mathbf{D}^r = 2\,\tilde{\mathbf{J}}^r\mathbf{W}\,\mathbf{J}^r$ but this assumes that the eigenvalues are linear functions of the force constants.[4] Also, if $\tilde{\mathbf{J}}^r\mathbf{W}\,\mathbf{J}^r$ is nearly singular the GNR method breaks down completely. Because equation (3) is often a good approximation to R near the minimum and because $\mathbf{H}^r$ is a better approximation to the inverse second derivatives of R than is $(2\tilde{\mathbf{J}}^r\mathbf{W}\,\mathbf{J}^r)^{-1}$ when the eigenvalues are markedly non-linear functions of the force constants, the FP method is generally more powerful than the GNR method.

I have tested the FP method for $n = 3$ using the A_1 symmetry factor of ClO_3F as a model, by refining the diagonal force constants with a wide range of arbitrarily chosen constant values for the off-diagonal force constants. In this case $f_i^r = F_{ii}^r$, **Z** is a unit matrix and can be ignored, and the elements of the square Jacobian are given by equation (5a) as $J_{kl}^r = (L_{ik}^r)^2$. **J** should be singular at the minimum. $\mathbf{H}^1$ was taken as the unit matrix, so the first iteration is one of steepest descent with $\mathbf{s}^1 = -\mathbf{g}^1$.

The procedure FLEPOMIN[5] (function MINimisation by the method of FLEtcher and POwell) was employed with trivial modifications and 12 digit floating point arithmetic was used throughout except that R was calculated as a double length inner product. The minimum R factor was thus derived to 12 significant figures. The force constant solutions obtained were independent of the initial values of F_{ii} to six significant figures. The method works equally well when the frequencies can be fitted exactly as when they cannot and is about equally as fast in both cases. I have found, however, that convergence is more rapid when the R factor is a function of frequencies such as $R^r = \sum^k (\nu_k - \nu_k^r)^2$ in which case

$$g_i^r = -\sum^k \left\{ \frac{130{\cdot}28\ \Delta\nu_k^r}{\sqrt{\lambda_k^r}} \left(\frac{\partial f_k}{\partial\lambda_i}\right)^r \right\}$$

Between 5 and 30 evaluations of this R factor are needed to minimise it, depending on the proximity of the initial force constants to the eventual solution. The time required to compute **f** by the FP method is thus comparable to that required by the GNR method. Moreover the notorious ill-conditioning of the latter is completely avoided since $\mathbf{D}^r$ is not singular at the minimum. By contrast, the spectral condition number of $\mathbf{J}^r$, defined as the square root of the ratio of the largest to smallest eigenvalue of $\mathbf{J}^r\tilde{\mathbf{J}}^r$, varied at the minima between *ca.* 1×10^5 and 1×10^7 compared

with a maximum of *ca.* 1×10^3 obtainable by the GNR method or modifications of it such as the "damped least squares" method.[6]

When R^{min} has been found, the transformation

$$\mathbf{F}^{\ddagger} = (\tilde{\mathbf{L}}^{min})^{-1} \mathbf{\Lambda} (\mathbf{L}^{min})^{-1} \quad (9)$$

provides an extremal set of force constants with which the frequencies are fitted exactly.[7] When $n > 2$ $\mathbf{F}^{\ddagger}$ is not unique but gives a limiting surface in force constant space within which the force constants are physically acceptable in that the frequencies are reproduced exactly. I believe that the use of the FP method [together with the transformation (9) if necessary and possible] will effectively solve the computational difficulties of force constant calculation, though it cannot, of course, solve the chemical difficulties associated with under-determined force fields and multiple solutions to the basic equation (1).

(*Received, September 17th,* **1970**; *Com.* **1586.**)

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