



GREEN'S FUNCTION DETERMINATION OF FORCE CONSTANTS—H₂O AS EXAMPLE

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Treating isotopically substituted molecule as a perturbed system, Green's function for the perturbation are constructed and related to the force field of vibration. By spectral representation, Green's function is diagonalized in the normal coordinates. Then transforming back to the Cartesian coordinates, the Cartesian force constants are generated without solving the secular equation directly. The relations between the internal force constants and the Cartesian force constants are given and complete internal force field can be obtained. The results for H₂O are discussed.

In the calculation of force constants of molecular vibration, the number of force constants to be determined is generally much larger than the number of vibrational frequencies available. Either additional informations, such as isotopical frequencies, or certain restricted models, such as Urey-Bradley field, valence-bond field, are used to render the calculation possible.

The complexity of this calculation in the internal coordinate system arises partially from the difficulty of setting the kinetic part of Hamiltonian. For a systemic approach, the well-known Wilson G-F matrix method is used by most authors.

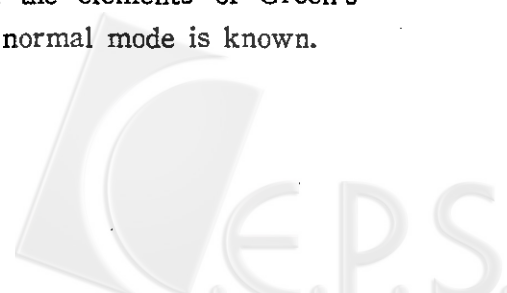
However, another approach exists. If we use Cartesian coordinate, to define Cartesian force constants, the Hamiltonian is also in quadratic form. Then, by calculating the complete force constants and finding transformation matrix between the Cartesian and the internal coordinates, the force constants in the internal coordinates can also be evaluated.

In the case of Cartesian coordinates, the number of force constants is greatly increased and the conditions of conservation of linear and angular momenta are usually impractical to apply unless we have known the detail forms of normal vibrations.

Instead of solving the secular equation explicitly, we use the Green's function method proposed by R. E. Dewames and T. Wolfram¹⁾, treating isotopically substituted molecules as perturbed system and constructing the Green's function of the system. A unique set of force constants is generated directly from the elements of Green's function once a certain parameter concerning the mixing of normal mode is known.

GENERAL FORMULATION

Define Q as a column vector:



$$Q = \begin{pmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_{3n} \end{pmatrix} \quad \begin{array}{l} \text{i. e. } Q_i = \sqrt{m_i} Z_i \\ Z_i \text{ is a cartesian coordinate} \\ m_i \text{ is the mass of atom} \end{array}$$

$\{Q_1, Q_2, \dots, Q_{3n}\}$ represent the mass weighted Cartesian coordinates. Then the vibration motion is determined by the secular equation:

$$\left[\frac{F_{ij}}{\sqrt{m_i m_j}} - \omega_i^2 \delta_{ij} \right] \begin{bmatrix} Q \end{bmatrix} = 0 \quad (1)$$

Where F_{ij} 's are the force constants, m_i is the mass of the i th atom, ω_i denotes the i th normal frequency, δ_{ij} is the Kronecker delta.

$$\text{Let } D = M^{-1/2} F M^{-1/2} \quad (2)$$

Eq. (1) becomes:

$$DQ = \omega^2 Q \quad (3)$$

M is a diagonal supermatrix with three 3×3 submatrices whose elements are the masses of atoms in the molecule.

$$\text{Let } Q = UN \quad (4)$$

N is a matrix of the normal coordinate and U is the transformation matrix between the normal coordinates and the mass weighted Cartesian coordinates. U_{ij} is the j th component (with mass weighted) of the normal coordinate whose eigenvalue is ω_i^2 .

In terms of U matrix, the dynamic matrix D can be expressed in spectral representation.

$$D = U^{-1} [\omega_i^2 \delta_{ij}] U \quad (5)$$

The only question now is to construct the U matrix. The complete force constants can be generated from U .

CONSTRUCTION OF NORMAL MODE

The normal coordinates for an unperturbed molecule can be constructed from the symmetry coordinates obtained by group theoretical method.

Let S be the symmetric coordinates

$$\text{and } S = LQ$$

$$N = AS$$

$$\text{then } N = ALQ$$

(6)

Comparing with Eq. (4), we get:



$$U=(AL)^{-1}=L'A' \quad (7)$$

While L' and A' denote the transpose matrices of L and A . The matrix L can be obtained by group theoretical method²⁾

$$S_k^{(\tau)}=\eta \sum_R X_R^{(\tau)} R Q_i \quad (8)$$

$S_k^{(\tau)}$ belongs to τ th symmetry species of the point group considered. $X_R^{(\tau)}$ is the character of τ th symmetry species for the symmetry operation R , and η is a normalization constant.

Then, the A matrix can be defined by the individual symmetry species as

$$N_i{}^\tau = \sum_j A_{ij}{}^{(\tau)} S_j^{(\tau)} \quad (9)$$

that is

$$A = \begin{pmatrix} A^{(1)} & 0 & 0 \\ 0 & A^{(2)} & \\ 0 & & A^{(n)} \end{pmatrix} \quad (10)$$

$A_{ij}{}^{(\tau)}$'s are the mixing parameters describing how the symmetry coordinates are mixed to form the normal coordinates in the τ th symmetry species. Once these mixing parameters are known, U -matrix can be generated and the complete force field can be calculated. We determined these parameters by treating isotopically substituted molecules as a perturbed system.

GREEN'S FUNCTION

For isotopically substituted molecule, the force field is considered unchanged,

$$F'=F \quad M'=M+\Delta M \quad (11)$$

Substituting Eq. (11) into the eigen equation of the perturbed system, we get:

$$[F-M\omega^2]Q'=\Delta M\omega^2Q' \quad (12)$$

or

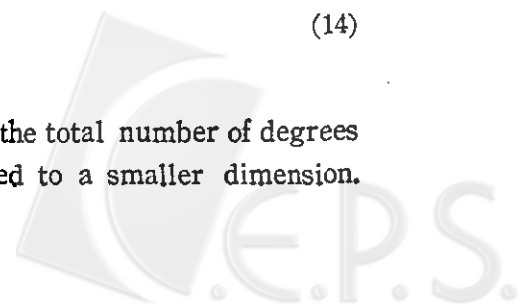
$$Q'=G(\omega^2)M^{-1}\Delta M\omega^2Q' \quad (13)$$

where $G(\omega^2)=(D-\omega^2)^{-1}$ is called the Green's function. From Eq. (13) one arrives at the determinant for the vibrational frequencies of the "perturbed" molecule in terms of Green's function.

$$|I-G(\omega^2)\Delta MM^{-1}\omega^2|=0 \quad (14)$$

while I is a unit matrix.

In general, the dimensionality of ΔM is much smaller than the total number of degrees of freedom and therefore the secular determinant is truncated to a smaller dimension.



One only needs the submatrix of G associated with the perturbation. In case of a single isotope substitution, the secular determinant reduces to

$$|I - \epsilon G(\omega^2)\omega^2| = 0 \quad (15)$$

while

$$\epsilon = \frac{(m^{(i)} - m)}{m} \quad (16)$$

$m^{(i)}$ is the mass of isotope.

By Eq. (5), the Green's function is easily constructed in the spectral representation.

$$G(\omega^2) = U \begin{pmatrix} \frac{1}{\omega_1^2 - \omega^2} & 0 & 0 \\ 0 & \frac{1}{\omega_2^2 - \omega^2} & 0 \\ 0 & 0 & \frac{1}{\omega_{3n}^2 - \omega^2} \end{pmatrix} U^{-1} \quad (17)$$

ω_i 's are frequencies for the unperturbed molecule including 6 zero frequencies associated with translational and rotational motion.

Substitution of Eq. (17) into Eq. (14) or Eq. (15), the parameters A_{ij} can be calculated and the complete force constants are generated by Eq. (5) without employing any special force field. We shall discuss the calculation in detail with triatomic molecule H_2O as an example.

APPLICATION TO BENT TRIATOMIC MOLECULE H_2O

A. Construction of U-matrix

Here we need only consider the inplan motions. The six mass weighted coordinates are shown in Fig. 1.

The six symmetry coordinates denoting vibration, translation and rotation in the molecular plan are shown in Fig. 2.

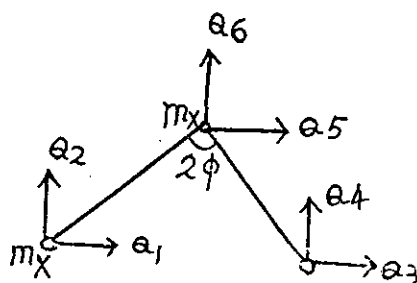
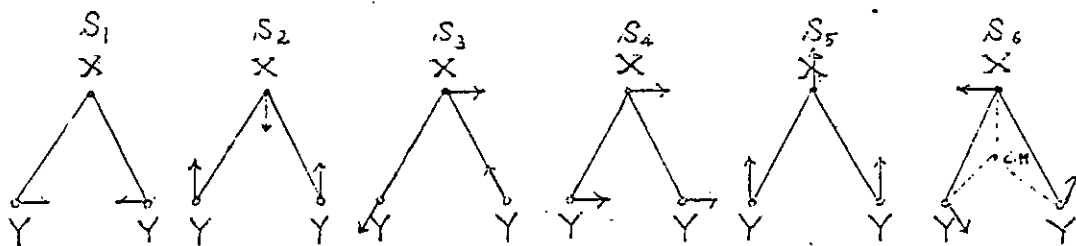


Fig 1




 Fig. 2. Symmetry coordinates for bent triatomic molecule XY_2

The symmetry coordinates S_1 and S_2 transform according to the same symmetry species A_1 and therefore normal coordinates will be linear combinations of S_1 and S_2

$$\begin{aligned} N_1 &= (S_1 + aS_2) (1+a^2)^{-1/2} \\ N_2 &= (S_2 - aS_1) (1+a^2)^{-1/2} \end{aligned} \quad (18)$$

The remaining symmetry coordinates are also normal coordinates. With Fig 1. and Fig 2. as aids and by the incorporation of Eq. (18), the U -matrix is easily constructed. In Table 1, the complete U -matrix is given.

 Table 1. U -matrix

| | | | | | |
|--------------------------------|-------------------------------|--------------------------------------|--------------------|--------------------|--|
| $1/\sqrt{2}C$ | $-a/\sqrt{2}C$ | $-(m_x)^{1/2}\sin\phi\mu_2/\sqrt{2}$ | $(m_y)^{1/2}\mu_1$ | 0 | $m_x\cos\phi\mu_1\mu_2/\sqrt{2}$ |
| $a(m_x)^{1/2}\mu_1/\sqrt{2}C$ | $(m_x)^{1/2}\mu_1/\sqrt{2}C$ | $-(m_x)^{1/2}\cos\phi\mu_2/\sqrt{2}$ | 0 | $(m_y)^{1/2}\mu_1$ | $-\sin\phi\mu_2/\sqrt{2}\mu_1$ |
| $-1/\sqrt{2}C$ | $a/\sqrt{2}C$ | $-(m_x)^{1/2}\sin\phi\mu_2/\sqrt{2}$ | $(m_y)^{1/2}\mu_1$ | 0 | $m_x\cos\phi\mu_1\mu_2/\sqrt{2}$ |
| $a(m_x)^{1/2}\mu_1/\sqrt{2}C$ | $(m_x)^{1/2}\mu_1/\sqrt{2}C$ | $(m_x)^{1/2}\cos\phi\mu_2/\sqrt{2}$ | 0 | $(m_y)^{1/2}\mu_1$ | $\sin\phi\mu_2/\sqrt{2}\mu_1$ |
| 0 | 0 | $\sqrt{2}(m_y)^{1/2}\sin\phi\mu_2$ | $(m_x)^{1/2}\mu_1$ | 0 | $\sqrt{2}(m_xm_y)^{1/2}\cos\phi\mu_1\mu_2$ |
| $-a\sqrt{2}(m_y)^{1/2}\mu_1/C$ | $-\sqrt{2}(m_y)^{1/2}\mu_1/C$ | 0 | 0 | $(m_x)^{1/2}\mu_1$ | 0 |

$$\mu_1 = (m_x + 2m_y)^{-1/2} \quad \mu_2 = (m_x + 2m_y\sin^2\phi)^{-1/2} \quad C^2 = (1+a^2)$$

B. Determination of mixing parameter

Consider isotope substitution $YXY \rightarrow Y^{(t)}XY^{(t)}$, M_y is changed into $M_y^{(t)}$. Then by substitution of the complete U -matrix into Eq. (17) and Eq. (15) one get.

$$\omega_1'^2\omega_2'^2 = \omega_1^2\omega_2^2 \left(\frac{m_y}{m_y'}\right)^2 \left(\frac{2m_y' + m_x}{2m_y + m_x}\right) \quad (19)$$

$$\omega_1'^2 + \omega_2'^2 = \frac{C^2(\omega_1^2 + \omega_2^2)(2m_y + m_x) + [(m_y/m_y') - 1][2m_yC^2\omega_2^2 + 2m_y\omega_1^2 + m_xC^2(\omega_1^2 + \omega_2^2)]}{C^2(2m_y + m_x)} \quad (20)$$

Eq. (19) is the well-known Teller-Redlich product rule. By Eq. (20) the mixing parameter "a" can be calculated once the frequencies for isotopically substituted molecule are known.

Table 2. Vibrational frequencies of H₂O and D₂O

| | 1 | 2 | 3 |
|------------------|---------|---------|---------|
| H ₂ O | 3825.32 | 1653.91 | 3935.59 |
| D ₂ O | 2758.06 | 1210.25 | 2883.79 |

With the frequencies listed in Table 2, the mixing parameter "a" is determined. $a=0.7217$.

C. Calculation of force constants

By Eq. (5) and Table 1, the force field is generated as:

$$F_{11} = \frac{\omega_1^2 m_y}{2C^2} + \frac{\omega_2^2 Q^2 m_y}{2C^2} + \omega_3^2 m_x m_y \sin^2 \phi \mu_2^2 / 2$$

$$F_{12} = a m_y (m_x)^{1/2} \mu_1 \omega_1^2 / 2C^2 - \omega_2^2 m_y (m_x)^{1/2} \mu_1 a / 2C^2 + [(m_x) \sin \phi \cos \phi \cdot \mu_2^2 \omega_3^2] / 2$$

$$F_{13} = -\frac{\omega_1^2 m_y}{2C^2} - \frac{a^2 \omega_2^2 m_y}{2C^2} + \omega_3^2 m_x m_y \sin^2 \phi \mu_2^2 / 2$$

$$F_{14} = \omega_1^2 m_y (m_x)^{1/2} a \mu_1 / 2C^2 - \omega_2^2 m_y (m_x)^{1/2} a \mu_1 / 2C^2 - (m_x m_y \sin \phi \cos \phi \mu_2^2 \omega_3^2) / 2$$

$$F_{15} = -m_x m_y \sin^2 \phi \mu_2^2 \omega_3^2$$

$$F_{16} = (\omega_2^2 - \omega_1^2) [a m_y (m_x)^{1/2} \mu_1 / C^2]$$

$$F_{22} = a^2 m_x m_y \mu_1^2 \omega_1^2 / 2C^2 + m_x m_y \mu_1^2 \omega_2^2 / 2C^2 + m_x m_y \cos^2 \phi \mu_2^2 \omega_3^2 / 2$$

$$F_{23} = [m_y (m_x)^{1/2} a \mu_1 / 2C^2] (\omega_2^2 - \omega_1^2) + m_x m_y \sin \phi \cos \phi \mu_2^2 \omega_3^2 / 2$$

$$F_{24} = a^2 m_x m_y \mu_1^2 \omega_1^2 / 2C^2 + m_x m_y \mu_1^2 \omega_2^2 / 2C^2 - m_x m_y \cos^2 \phi \mu_2^2 \omega_3^2 / 2$$

$$F_{25} = -m_x m_y \sin \phi \cos \phi \mu_2^2 \omega_3^2$$

$$F_{26} = -a^2 m_x m_y \mu_1^2 \omega_1^2 / C^2 - m_x m_y \mu_1^2 \omega_2^2 / C^2$$

$$F_{35} = 2m_x m_y \sin^2 \phi \mu_2^2 \omega_3^2$$

$$F_{36} = 2a^2 m_x m_y \mu_1^2 \omega_1^2 / C^2 + 2m_x m_y \mu_1^2 \omega_2^2 / C^2$$

While $F_{33}=F_{11}$ $F_{34}=-F_{12}$ $F_{35}=F_{15}$ $F_{36}=-F_{16}$ $F_{44}=F_{22}$ $F_{45}=-F_{25}$ $F_{46}=F_{26}$ $F_{56}=0$ by symmetry consideration.

The force constants calculated are listed in Table 3.

D. Internal force constants

Once the Cartesian force constants are calculated, one can transform them to internal coordinates, and find the internal force constants. We calculate the force constants of H₂O and compare them to the results of other authors.

Define the internal force field of XYX molecule as

$$2V = f_r \Delta r_1^2 + f_r \Delta r_2^2 + 2f_{rr} \Delta r_1 \Delta r_2 + \frac{f_\phi}{r^2} (\Delta \phi)^2 + 2 \frac{f_{r\phi}}{r} \Delta r_1 \Delta \phi + 2 \frac{f_{r\phi}}{r} \Delta r_2 \Delta \phi \quad (21)$$

r_1, r_2 —bond distances of X—Y bonds

2ϕ —bond angle of X—Y—X

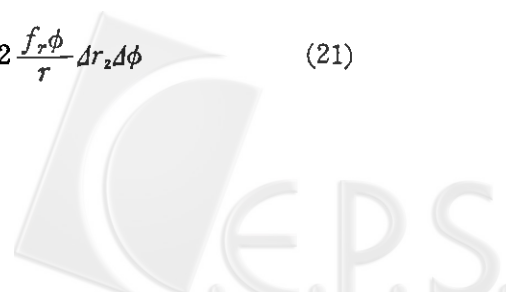


Table 3. Force constants of H₂O. F_{ij} in 10⁵ dyne/cm

| | | | | | |
|----------|----------|----------|----------|----------|----------|
| F_{11} | F_{12} | F_{13} | F_{14} | F_{15} | F_{16} |
| 5.796 | 3.641 | -0.470 | -0.689 | -0.584 | -3.158 |
| F_{21} | F_{22} | F_{23} | F_{24} | F_{25} | F_{26} |
| 3.641 | 3.392 | 0.689 | 0.197 | -4.125 | -3.589 |
| F_{31} | F_{32} | F_{33} | F_{34} | F_{35} | F_{36} |
| -0.470 | 0.689 | 5.796 | -3.641 | -0.584 | 3.158 |
| F_{41} | F_{42} | F_{43} | F_{44} | F_{45} | F_{46} |
| -0.689 | 0.197 | -3.641 | 3.392 | 4.125 | -3.589 |
| F_{51} | F_{52} | F_{53} | F_{54} | F_{55} | F_{56} |
| -0.584 | -4.125 | -0.584 | 4.125 | 10.652 | 0 |
| F_{61} | F_{62} | F_{63} | F_{64} | F_{65} | F_{66} |
| -3.158 | -3.589 | 3.158 | -3.589 | 0 | 16.829 |

The relations between the internal force constants and the Cartesian force constants are:

$$\begin{aligned}
 f_r &= F_{11}\sin^2\phi + F_{22}\cos^2\phi + 2F_{12}\sin\phi\cos\phi \\
 f_{rr} &= F_{24}\cos^2\phi - F_{13}\sin^2\phi - 2F_{23}\sin\phi\cos\phi \\
 \frac{f_\phi}{r^2} &= F_{11}\cos^2\phi + F_{22}\sin^2\phi - 2F_{12}\sin\phi\cos\phi \\
 \frac{f_{r\phi}}{r} &= (F_{11} - F_{22})\sin\phi\cos\phi + F_{12}(\cos^2\phi - \sin^2\phi)
 \end{aligned}
 \tag{22}$$

The force constants of H₂O calculated in this way are listed in Table 4.

These results are compared to the results of (3) various force field model listed by D. E. Freeman in Table 5.

Table 4. Internal force constants of H₂O (in 10⁵ dyne/cm)

| f_r | f_{rr} | $\frac{f_\phi}{r^2}$ | $\frac{f_{r\phi}}{r}$ |
|-------|----------|----------------------|-----------------------|
| 8.420 | -0.299 | 0.7678 | 0.2532 |

Table 5. Comparison of Force fields for water (in dyne/cm)

| Character of Force field | f_r | $\frac{f}{r^2}$ | f_{rr} | $\frac{f_r}{r}$ |
|--------------------------|-------|-----------------|----------|-----------------|
| 1. (TrF) _{max} | 8.443 | 0.785 | -0.107 | 0.388 |
| 2. (TrF') _{max} | 8.445 | 0.791 | -0.110 | 0.414 |
| 3. Progressive rigidity | 8.444 | 0.750 | -0.111 | 0.044 |
| 4. (TrL) _{max} | 8.452 | 0.754 | -0.103 | 0.159 |
| 5. This Work | 8.420 | 0.768 | -0.299 | 0.2532 |

Although the value of f_r is a little bit smaller, the results seem justified in comparison to the results of other force field model.

In more complex molecule, if there is more mixing in the symmetry coordinates, we need several isotopes to calculate the mixing parameters. In this case, the method of perturbation still applies, but the off-diagonal terms in force field are sensitive to the variation of α -value. Nonetheless, the Green's function method has several advantages. First, no restrictions are put on the force field model. In larger molecule, the calculation is not so complex as direct solution of secular equation. And the knowledge of mixing parameters lead to a fuller appreciation of the normal vibrations.

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