# The anharmonic infrared spectra of polycyclic aromatic hydrocarbons
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# Linear transformation of anharmonic molecular force constants between normal and Cartesian coordinates

A full derivation of the analytic transformation of the quadratic, cubic, and quartic force constants from normal coordinates to Cartesian coordinates is given. Previous attempts at this transformation have resulted in non-linear transformations, however for the first time a simple linear transformation is presented here. Two different approaches have been formulated and implemented, one of which does not require prior knowledge of the translation-rotation eigenvectors from diagonalization of the Hessian matrix. The validity of this method is tested using two molecules $H_2O$ and c-$C_3H_2D^+$.

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## 2.1 Introduction

Over the past 25-30 years, quartic force fields (QFFs) have been used extensively to compute fundamental molecular vibrational frequencies, combination and overtone bands, and rovibrational spectroscopic constants (for example, see Refs. 56, 57, 58, 59, 60, 61, 62, 63 and references therein). QFFs have been used extensively in both second-order perturbation theory [64, 65, 66, 67] and variational treatments [68, 69, 70] to solve the bound-state nuclear Schrödinger equation. QFFs are usually computed in simple- or symmetry-internal coordinates and then transformed into either normal coordinates for perturbation theory analysis or some sort of Morse-cosine coordinate system for variational treatments. [71, 72] This allows one to compute the vibrational frequencies and rovibrational spectroscopic constants for all isotopologues. However, it was noted in a 1989 paper by Schneider and Thiel [73] that since the second-order perturbation theory formula only uses a subset of the quartic force constants in the normal coordinate basis, if one were to use central differences of analytical second derivative techniques, that many fewer displacements would be needed if displacements were made in normal coordinates, and only those quartic force constants needed were computed. One disadvantage to this approach is that since normal coordinates are mass-dependent, the resulting normal coordinate partial QFF will yield vibrational frequencies and rovibrational spectroscopic constants for only the isotopologue used to define the normal coordinates used to define the displacements.

Nonetheless, if one has the full or only a partial QFF in normal coordinates, there are good reasons to transform the QFF into Cartesian coordinates. For example, also in 1989, Thiel[55] showed how to transform the normal coordinate force constants into Cartesian coordinates in order to represent the QFF in simple internal or symmetry internal coordinates which may then be used in the spectroscopic analysis of an isotopologue or they may be transferred to molecular systems with a similar internal coordinate(s) in the approximate construction of a quadratic, cubic, or quartic force field of a larger molecule.

It has been shown in the literature that the transformation from Cartesian coordinate to normal coordinate force constants is a linear transformation [74]. However, the opposite transformation, from normal coordinate to Cartesian coordinate force constants, has until now only been dealt with in the literature as a non-linear transformation [55, 75]. The reason for the transformation to be thought as linear one way but non-linear the other way is due to the number of defined coordinates in the respective coordinate systems. The Cartesian coordinates that define the positions of the atoms in a molecule have 3N unique degrees of freedom (where N is the number of atoms) whereas normal coordinates that define the position of the atoms have 3N-6 coordinates (3N-5 in linear molecules). When moving from Cartesian coordinates to normal coordinates the loss of the six (five) degrees of freedom occurs because normal coordinates are defined in such a way that the origin of the coordinate system moves and rotates with the center of mass of the molecule, effectively eliminating the need for the six rotational and translational normal modes. This does not affect the transformation of the force constants from 3N Cartesian coordinates to 3N-6 normal coordinates since the loss of the six extra degrees of freedom have no effect on the transformation. However, when transforming from normal coordinates to Cartesian coordinates the process involves going up from 3N-6 normal coordinates to 3N Cartesian coordinates. This increase in the number of coordinates was the reason for the need of the previous non-linear transformation.

The previously non-linear method, as mentioned above, involves the calculation of many terms including mixed partial derivatives of the second and third order (which themselves involve the calculation of another six additional sets of terms, including Coriolis constants). These terms arise precisely because the rotational and translational normal modes are not included in the transformation. This highly complicated non-linear transformation can be greatly simplified into a linear transformation if the rotational and translational normal modes are re-introduced. In this way all of the Coriolis terms and mixed partial derivatives become precisely zero, eliminating these non-linear terms in the previously derivation. This work outlines the method, effectively making the transformation from normal coordinate force constants to Cartesian coordinate force constants a simple linear 3N to 3N coordinate conversion. §2.2 shows the normal mode eigenvectors derivation as well as gives two methods to regenerate the missing translational and rotational normal mode eigenvectors. §2.3 derives the linear transformation equations for the conversion of the quadratic, cubic, and quartic force constants forwards and backwards between Cartesian and normal coordinates. §2.4 derives the partial derivatives needed in §2.3. §2.5 outlines two separate mathematical manipulations that can be implemented to speed up calculation time of the transformation. Finally §2.6 applies the transformation method described in this paper to two example molecules, $H_2O$ and c-$C_3H_2D^+$, to show the validity of the method.

## 2.2 Derivation of the eigenvectors

The Hamiltonian for a molecule can be written using a Taylor expansion for the potential energy function as follows

$$\begin{aligned}\mathcal{H} = &-\frac{\hbar^2}{2}\sum_{a=1}^{3N}\frac{\partial^2}{\partial Y_a^2} + V_0\\ &+\sum_{a=1}^{3N}\left(\frac{\partial V}{\partial Y_a}\right)_0 Y_a\\ &+\frac{1}{2}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\left(\frac{\partial^2 V}{\partial Y_a \partial Y_b}\right)_0 Y_a Y_b + \cdots\end{aligned} \tag{2.1}$$

where the $x,y,z$ coordinates of the atoms are numbered from 1 to 3N, and $Y_a = \sqrt{m_a}X_a$ is the mass-weighted Cartesian coordinate of a given atom

The harmonic approximation is made by retaining only the first non-vanishing term of its Taylor expansion ($V_0$ is arbitrary so it is set to zero and since the Taylor expansion is taken at a stationary point any gradients are also zero).

$$\mathcal{H} = -\frac{\hbar^2}{2}\sum_{a=1}^{3N}\frac{\partial^2}{\partial Y_a^2} + \frac{1}{2}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\left(\frac{\partial^2 V}{\partial Y_a \partial Y_b}\right)_0 Y_a Y_b \tag{2.2}$$

To solve for the normal mode eigenvalues (frequencies) of the molecule the mass-weighted Hessian is diagonalized by

$$\boldsymbol{\Omega}^T \boldsymbol{F} \boldsymbol{\Omega} = \boldsymbol{f} \tag{2.3}$$

where $\boldsymbol{F}_{(a,b)}$ is the mass-weighted Hessian that consists of the second order derivatives of the potential energy

$$F_{a,b} = \left(\frac{\partial^2 V}{\partial Y_a \partial Y_b}\right)_0 \tag{2.4}$$

and $\boldsymbol{f} = diag(f_1, f_2, ..., f_{3N-6}, 0, 0, 0, 0, 0, 0)$ are the frequencies of the normal modes. The last six zero frequencies correspond to the rotational and translational modes of the non-linear molecule at its stationary point. The columns that make up the $\boldsymbol{\Omega}$ matrix are the normal mode eigenvectors $\boldsymbol{\omega}$ expressed in mass-weighted Cartesian coordinates. The last six columns correspond to the translational and rotational eigenvectors, but in reality can be linear combinations of these six eigenvectors and as such may not be easily visualized.

Generally only the non-zero frequency modes of the $\boldsymbol{\Omega}$ matrix and their corresponding eigenvectors $\boldsymbol{\omega}$ are reported in the literature or in the default output of computational packages. The rotational and translational eigenvectors are normally dropped, resulting in only the non-zero 3N-6 normal modes (3N-5 for linear molecules) being reported. However, these six (five) normal mode eigenvectors are needed to make the transformation from normal coordinate to Cartesian coordinate force constants linear. In such cases the translational and rotational eigenvectors can be regenerated by re-diagonalizing the mass-weighted Hessian as in equation 2.3, or by explicitly regenerating the missing mass-weighted eigenvectors as shown below. Note that when regenerating the six 'missing' eigenvectors as shown in this work, they will represent the pure rotational and translational eigenvectors and will be easily visualized as such, unlike the linearly combined eigenvectors that result from the numerical re-diagonalization method. It should be noted that the resulting individual Cartesian coordinate force constants obtained with these two methods may differ due to the degenerate nature of Cartesian coordinates, but will produce Cartesian coordinate force constants that are equivalent when taken as full sets. There are two sources of degeneracy when it comes to Cartesian force constants: One being the arbitrary orientation and position chosen for the molecule in the Cartesian plane, the other being the infinite number of linear combinations of the rotational and translational eigenvectors. One should also be cautious when re-diagonalizing the Hessian of a molecule with degenerate modes. The eigenvectors for degenerate vibrational modes can be arbitrarily rotated amongst each other which will give different self-consistent cubic and quartic force constants. Hence, if re-diagonalizing, one needs to ensure degenerate modes are aligned the way they were when the normal coordinate force constants were generated. For this reason it would be advantageous to use the regeneration method for molecules with degenerate modes.

The missing eigenvectors can be regenerated using the methods extracted from Ref. 76. The translational eigenvectors can be written as follows

$$\omega_{(3N-5)} = [\sqrt{m_1}, 0, 0, \sqrt{m_2}, 0, 0, \ \dots\ , \sqrt{m_N}, 0, 0] \tag{2.5}$$

$$\omega_{(3N-4)} = [0, \sqrt{m_1}, 0, 0, \sqrt{m_2}, 0, \ \dots\ , 0, \sqrt{m_N}, 0] \tag{2.6}$$

$$\omega_{(3N-3)} = [0, 0, \sqrt{m_1}, 0, 0, \sqrt{m_2}, \ \dots\ , 0, 0, \sqrt{m_N}] \tag{2.7}$$

The rotation eigenvectors components can be written as follows

$$\omega_{(3N-2)_{j,i}} = \left[(P_y)_i D_{j,3} - (P_z)_i D_{j,2}\right] \times \sqrt{m_i} \tag{2.8}$$

$$\omega_{(3N-1)_{j,i}} = \left[(P_z)_i D_{j,1} - (P_x)_i D_{j,3}\right] \times \sqrt{m_i} \tag{2.9}$$

$$\omega_{(3N)_{j,i}} = \left[(P_x)_i D_{j,2} - (P_y)_i D_{j,1}\right] \times \sqrt{m_i} \tag{2.10}$$

where $\mathbf{D}$ is the matrix that diagonalizes the moment of inertial tensor and $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ are defined as

$$\mathbf{P}_x = [\mathbf{X}_1 \cdot \mathbf{D}_x, \mathbf{X}_2 \cdot \mathbf{D}_x, \ \dots\ , \mathbf{X}_n \cdot \mathbf{D}_x] \tag{2.11}$$

$$\mathbf{P}_y = [\mathbf{X}_1 \cdot \mathbf{D}_y, \mathbf{X}_2 \cdot \mathbf{D}_y, \ \dots\ , \mathbf{X}_n \cdot \mathbf{D}_y] \tag{2.12}$$

$$\mathbf{P}_z = [\mathbf{X}_1 \cdot \mathbf{D}_z, \mathbf{X}_2 \cdot \mathbf{D}_z, \ \dots\ , \mathbf{X}_n \cdot \mathbf{D}_z] \tag{2.13}$$

where $\mathbf{X}_n$ is the Cartesian coordinate vector of the n$^{th}$ atom, and $\mathbf{D}_\alpha$ is the $\alpha^{th}$ row of the $\mathbf{D}$ matrix.

All of the eigenvectors are then normalized to produce an orthonormal set of 3N eigenvectors $\mathbf{\Omega}$. Note that in the linear molecule case one of the rotational eigenvectors will come out as the zero vector, and should be dropped.

## 2.3 Derivation of the transformations equations

In the quartic force field approximation the potential energy of the Hamiltonian takes the form of the first three non-zero terms in its Taylor expansion

$$\begin{aligned}\mathcal{H} = &-\frac{\hbar^2}{2}\sum_{a=1}^{3N}\frac{\partial^2}{\partial Y_a^2} + \frac{1}{2}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\left(\frac{\partial^2 V}{\partial Y_a \partial Y_b}\right)_0 Y_a Y_b \\ &+ \frac{1}{6}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\sum_{c=1}^{3N}\left(\frac{\partial^3 V}{\partial Y_a \partial Y_b \partial Y_c}\right)_0 Y_a Y_b Y_c \\ &+ \frac{1}{24}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\sum_{c=1}^{3N}\sum_{d=1}^{3N}\left(\frac{\partial^4 V}{\partial Y_a \partial Y_b \partial Y_c \partial Y_d}\right)_0 Y_a Y_b Y_c Y_d\end{aligned} \tag{2.14}$$

Instead of solving this Hamiltonian directly, second-order perturbation theory is often used. The quadratic force constants are used in the unperturbed harmonic terms, the cubic force constants are used in the first term of the perturbation, and the quartic force constants are used in the second term of the perturbation. Therefore it will be shown how to transform these three orders of force constants between normal and Cartesian coordinates. It will also be easy to see how the transformations can be extended to any number of orders. In order to convert the force constants between the two coordinate systems, the Taylor expansions of the potential in each coordinate system are considered. The potential energy function in Cartesian coordinates is given by

$$\begin{aligned}V_{cart} = &\frac{1}{2}\sum_{a=1}^{3N}\sum_{b=1}^{3N} F_{ab} X_a X_b \\ &+ \frac{1}{6}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\sum_{c=1}^{3N} F_{abc} X_a X_b X_c \\ &+ \frac{1}{24}\sum_{a=1}^{3N}\sum_{b=1}^{3N}\sum_{c=1}^{3N}\sum_{d=1}^{3N} F_{abcd} X_a X_b X_c X_d\end{aligned} \tag{2.15}$$

where $\mathrm{F}_{ab}$, $\mathrm{F}_{abc}$ and $\mathrm{F}_{abcd}$ the Cartesian quadratic, cubic, and quartic force constants respectively.

Likewise, the potential energy function in normal coordinates is given by

$$\begin{aligned}V_{norm} = &\frac{1}{2}\sum_{k=1}^{3N}\sum_{l=1}^{3N} \Phi_{kl} Q_k Q_l \\ &+ \frac{1}{6}\sum_{k=1}^{3N}\sum_{l=1}^{3N}\sum_{m=1}^{3N} \Phi_{klm} Q_k Q_l Q_m \\ &+ \frac{1}{24}\sum_{k=1}^{3N}\sum_{l=1}^{3N}\sum_{m=1}^{3N}\sum_{n=1}^{3N} \Phi_{klm} Q_k Q_l Q_m Q_n\end{aligned} \tag{2.16}$$

where $\Phi_{kl}$, $\Phi_{klm}$ and $\Phi_{klmn}$ are the normal coordinate quadratic, cubic, and quartic force constants respectively.

Since the total potential energy of a molecule is independent of the coordinate system used, it can be written that

$$V_{cart} = V_{norm} \tag{2.17}$$

Subsequently, all derivatives of the total potential energy in any two different coordinate systems with respect to *same coordinate system* are also equal.

Taking the second derivatives of equations 2.15 and 2.16 with respect to $X_a$ and $X_b$ gives the following:

$$\begin{aligned}\left(\frac{\partial^2 V_{cart}}{\partial X_a \partial X_b}\right) &= \frac{1}{2}F_{ab} + \frac{1}{2}F_{ba} \\ &= F_{ab}\end{aligned} \tag{2.18}$$

and

$$\begin{aligned}\left(\frac{\partial^2 V_{norm}}{\partial X_a \partial X_b}\right) &= \frac{1}{2}\sum_{k=1}^{3N}\sum_{l=1}^{3N}\Phi_{kl}\left[\frac{\partial Q_k}{\partial X_a}\frac{\partial Q_l}{\partial X_b} + \frac{\partial Q_k}{\partial X_b}\frac{\partial Q_l}{\partial X_a}\right. \\ &\quad \left. + \frac{\partial^2 Q_k}{\partial X_a \partial X_b}Q_l + \frac{\partial^2 Q_l}{\partial X_a \partial X_b}Q_k\right] \\ &= \sum_{k=1}^{3N}\sum_{l=1}^{3N}\Phi_{kl}\left[\frac{\partial Q_k}{\partial X_a}\frac{\partial Q_l}{\partial X_b}\right]\end{aligned} \tag{2.19}$$

respectively.

When expressions 2.18 and 2.19 are equated it gives the transformation equation for going from normal coordinates to Cartesian coordinates for the quadratic force constant terms. A similar procedure is performed on equations 2.15, and 2.16, but with a third derivative with respect to $X_c$, and a third and forth derivative with respect to $X_c$ and $X_d$ respectively, to give the following set of transformations.

$$F_{ab} = \sum_{k=1}^{3N}\sum_{l=1}^{3N}\Phi_{kl}\left[\frac{\partial Q_k}{\partial X_a}\frac{\partial Q_l}{\partial X_b}\right] \tag{2.20}$$

$$F_{abc} = \sum_{k=1}^{3N}\sum_{l=1}^{3N}\sum_{m=1}^{3N}\Phi_{klm}\left[\frac{\partial Q_k}{\partial X_a}\frac{\partial Q_l}{\partial X_b}\frac{\partial Q_m}{\partial X_c}\right] \tag{2.21}$$

$$F_{abcd} = \sum_{k=1}^{3N}\sum_{l=1}^{3N}\sum_{m=1}^{3N}\sum_{n=1}^{3N}\Phi_{klmn}\left[\frac{\partial Q_k}{\partial X_a}\frac{\partial Q_l}{\partial X_b}\frac{\partial Q_m}{\partial X_c}\frac{\partial Q_n}{\partial X_d}\right] \tag{2.22}$$

Note that the summations are over all of the 3N normal modes, including translational and rotational modes. If the translational and rotational modes were neglected then the higher order mixed derivatives (not shown here) would be non-zero, resulting in the non-linear transformation mentioned above.

The derivation for the opposite transformation, going from Cartesian to normal coordinate force constants, is the same procedure as above except the derivatives are taken with respect to $Q_k$, $Q_l$, $Q_m$, and $Q_n$. This gives

$$\Phi_{kl} = \sum_{a=1}^{3N} \sum_{b=1}^{3N} F_{ab} \left[ \frac{\partial X_a}{\partial Q_k} \frac{\partial X_b}{\partial Q_l} \right] \tag{2.23}$$

$$\Phi_{klm} = \sum_{a=1}^{3N} \sum_{b=1}^{3N} \sum_{c=1}^{3N} F_{abc} \left[ \frac{\partial X_a}{\partial Q_k} \frac{\partial X_b}{\partial Q_l} \frac{\partial X_c}{\partial Q_m} \right] \tag{2.24}$$

$$\Phi_{klmn} = \sum_{a=1}^{3N} \sum_{b=1}^{3N} \sum_{c=1}^{3N} \sum_{d=1}^{3N} F_{abcd} \left[ \frac{\partial X_a}{\partial Q_k} \frac{\partial X_b}{\partial Q_l} \frac{\partial X_c}{\partial Q_m} \frac{\partial X_d}{\partial Q_n} \right] \tag{2.25}$$

## 2.4 Deriving the partial derivatives

The derivatives in equations 2.20 through 2.25 are generated from the 3N normal mode eigenvectors. First the mass weighting of the eigenvector matrix, $\mathbf{\Omega}$, is removed and each column vector is re-normalized

$$\bar{\mathbf{\Omega}} = \left( \mathbf{M}^{-\frac{1}{2}} \mathbf{\Omega} \right) \mathbf{\Lambda} \tag{2.26}$$

where $\mathbf{M} = diag(m_1, m_2, ..., m_N)$ and $\mathbf{\Lambda}$ is a diagonal matrix containing the normalization factor for each respective mass-unweighted eigenvector.

Each normal mode vector $\boldsymbol{\omega}_N$ which are the components of $\bar{\mathbf{\Omega}}$ is then divided by the square root of its reduced mass $\mu_N$

$$\tilde{\mathbf{\Omega}} = \bar{\mathbf{\Omega}} \boldsymbol{\mu}^{-\frac{1}{2}} \tag{2.27}$$

where $\boldsymbol{\mu} = diag(\mu_1, \mu_2, ..., \mu_N)$ with

$$\mu_N = \sum_i m_{N,i} \omega_{N,i}^2 \tag{2.28}$$

where $\omega_{N,i}$ is the i$^{th}$ component of eigenvector $\boldsymbol{\omega}_N$ and $m_{N,i}$ is the corresponding mass of i$^{th}$ component of eigenvector $\boldsymbol{\omega}_N$

This matrix $\tilde{\mathbf{\Omega}}$ is then a matrix of the values of the partial derivatives in equations 2.23 through 2.25 that are needed for the transformation from Cartesian to normal coordinate force constants.

$$\frac{\partial X_b}{\partial Q_l} = \tilde{\Omega}_{b,l} \tag{2.29}$$

The inverse of this matrix is then a matrix of the values of the partial derivatives in equations 2.20 through 2.22 that are needed for the transformation from normal coordinate to Cartesian coordinate force constants.

$$\frac{\partial Q_l}{\partial X_b} = \tilde{\Omega}^{-1}_{b,l} = \check{\Omega}_{l,b} \tag{2.30}$$

To reduce computational demand it is also possible to take advantage of the fact that the matrix $\bar{\boldsymbol{\Omega}}$ is orthonormal, which means $\bar{\boldsymbol{\Omega}}^{-1} = \bar{\boldsymbol{\Omega}}^{T}$. This can be used to avoid taking the inverse of the potentially large non-orthonormal $3N \times 3N$ matrix as is stated in equation 2.30. $\check{\boldsymbol{\Omega}}$ can instead be expressed as follows

$$\begin{aligned} \check{\boldsymbol{\Omega}} &= \tilde{\boldsymbol{\Omega}}^{-1} \\ &= \left(\bar{\boldsymbol{\Omega}}\boldsymbol{\mu}^{-\frac{1}{2}}\right)^{-1} \\ &= \boldsymbol{\mu}^{\frac{1}{2}}\bar{\boldsymbol{\Omega}}^{-1} \\ &= \boldsymbol{\mu}^{\frac{1}{2}}\bar{\boldsymbol{\Omega}}^{T} \end{aligned} \tag{2.31}$$

Both the inverse and transpose methods, equations 2.30 and 2.31 respectively, have been verified as numerically equivalent.

Furthermore, it can now be seen why the transformation from normal coordinate force constants to Cartesian coordinate force constants had previously been thought of as a non-linear transformation. Without the six additional rotational and translational normal modes added back into the $\boldsymbol{\Omega}$ matrix it is not possible to perform a standard inverse on the previously non-square $3N \times (3N - 6)$ normal mode matrix.

## 2.5 Implementation details

These transformations can be quite computationally demanding, especially with large molecules, since they are converting $(3N)^4$ values for the quartic force terms. To avoid nested summations the conversion equations can be broken up into a series of sequential summations. We thus have for the quadratic force constants:

$$F_{aj} = \sum_{i=1}^{3N} \check{\Omega}_{a,i} Q_{i,j} \tag{2.32}$$

$$F_{ab} = \sum_{j=1}^{3N} \check{\Omega}_{b,j} F_{a,j} \tag{2.33}$$

for the cubic force constants:

$$F_{ajk} = \sum_{i=1}^{3N} \check{\Omega}_{a,i} Q_{i,j,k} \tag{2.34}$$

$$F_{abk} = \sum_{j=1}^{3N} \check{\Omega}_{b,j} F_{a,j,k} \tag{2.35}$$

$$F_{abc} = \sum_{k=1}^{3N} \check{\Omega}_{c,k} F_{a,b,k} \tag{2.36}$$

and for the quartic force constants:

$$F_{ajkl} = \sum_{i=1}^{3N} \check{\Omega}_{a,i} Q_{i,j,k,l} \tag{2.37}$$

$$F_{abkl} = \sum_{j=1}^{3N} \check{\Omega}_{b,j} F_{a,j,k,l} \tag{2.38}$$

$$F_{abcl} = \sum_{k=1}^{3N} \check{\Omega}_{c,k} F_{a,b,k,l} \tag{2.39}$$

$$F_{abcd} = \sum_{l=1}^{3N} \check{\Omega}_{d,l} F_{a,b,c,l} \tag{2.40}$$

where $F_{a,\ldots,j,\ldots}$ are the intermediate mixed normal-Cartesian coordinate force constants calculated from the previous step.

## 2.6 Application to $H_2O$ and c-$C_3H_2D^+$

In this section the linear transformation method described in this paper is tested on two molecules $H_2O$ and c-$C_3H_2D^+$. Cartesian coordinate force constants are not unique for a given molecule (due to the infinite number of valid translational and rotational eigenvector sets) so direct comparison of the individual Cartesian force constants is not possible between different references. Instead two tests can be applied to check the validity of the transformation method. The first test is a forward transformation of the force constants from normal to Cartesian coordinates followed by a backwards transformation to obtain the same original values. The second test would use a set of reference force constants that were numerically calculated in both normal coordinates and Cartesian coordinates, transform the normal coordinate force constants to Cartesian coordinates, and then perform a second-order perturbation treatment using the original Cartesian force constants and finally comparing the results with a second-order perturbation treatment using the transformed Cartesian coordinates.

The first test was performed on the $H_2O$ molecule. Table 2.1 lists the full non-zero set of the original normal coordinate force constants of $H_2O$ as reported by Gaussian09[53] (B3LYP/4-31G) and the transformed values for each of the methods: the explicitly regeneration of the rotational and translational eigenvectors method (explicit), and the re-diagonalization of the Hessian method (re-diag). Six significant digits are available for the normal mode eigenvectors calculated by Gaussian09, and so are the limiting numerical factor in these transformations. It can therefore be seen that the resulting values from these tests all agree within the

| Normal coordinate quadratic force constants | | | |
|---|---|---|---|
| I,J | Gaussian09 | Explicit | Re-diag |
| 1,1 | 0.588920 | 0.5889195204 | 0.5889195204 |
| 2,2 | 0.556360 | 0.5563597083 | 0.5563597083 |
| 3,3 | 0.103107 | 0.1031073853 | 0.1031073853 |

| Normal coordinate cubic force constants | | | |
|---|---|---|---|
| I,J,K | Gaussian09 | Explicit | Re-diag |
| 2,1,1 | -1.537841 | -1.5378412008 | -1.5378412008 |
| 2,2,2 | -1.494314 | -1.4943140745 | -1.4943140745 |
| 3,1,1 | 0.147698 | 0.1476983577 | 0.1476983577 |
| 3,2,2 | 0.041158 | 0.0411582366 | 0.0411582366 |
| 3,3,2 | 0.109423 | 0.1094229743 | 0.1094229743 |
| 3,3,3 | -0.061993 | -0.0619934648 | -0.0619934648 |

| Normal coordinate quartic force constants | | | |
|---|---|---|---|
| I,J,K,L | Gaussian09 | Explicit | Re-diag |
| 1,1,1,1 | 3.743561 | 3.7435605526 | 3.7435605526 |
| 2,2,1,1 | 3.604032 | 3.6040318012 | 3.6040318012 |
| 2,2,2,2 | 3.484090 | 3.4840896130 | 3.4840896130 |
| 3,2,1,1 | -0.366798 | -0.3667977452 | -0.3667977452 |
| 3,2,2,2 | -0.191875 | -0.1918745935 | -0.1918745935 |
| 3,3,1,1 | -0.755795 | -0.7557945848 | -0.7557945848 |
| 3,3,2,2 | -0.611669 | -0.6116693020 | -0.6116693020 |
| 3,3,3,2 | 0.201451 | 0.2014514506 | 0.2014514506 |
| 3,3,3,3 | -0.051939 | -0.0519393906 | -0.0519393906 |

Table 2.1 Non-zero normal coordinate force constants of $H_2O$ before and after transformation from normal force constants and back to Cartesian coordinate force constants using the two methods for obtaining the missing eigenvectors, explicitly regenerating the rotational and translational eigenvectors, and re-diagonalizing the Hessian.

numerical accuracy available. The ‘explicit’ and ‘re-diag’ values are reported to ten decimal places to show agreement between the two transformation methods.

For the second test the c-$C_3H_2D^+$ QFF, as described in reference 77, is used. They calculated both the Cartesian coordinate and normal coordinate force constants and supplied those values for this paper. Three sets of Cartesian force constants are used for this test: the original Cartesian force constants from reference 77 are used as reference, the ‘explicit’ transformation method of this work using the normal coordinate QFF of reference 77, and finally the Hessian ‘re-diag’ transformation method of this work using the normal coordinate QFF of reference 77. Each of these sets of Cartesian coordinate force constants is used to perform a second-order perturbation theory (VPT2) analysis using SPECTRO[54]. All values should agree between the reference of reference 77 and the two VPT2 methods using the transformation here presented. Table 2.2 shows the resulting band positions and the resonances obtained by SPECTRO. Again, it can be seen that all values match within numerical accuracy. The position of the fundamental modes and spectroscopic constants obtained with the VPT2 implementation also agree, with numerical accuracy, between the reference and transformation method values.

These two tests show that the transformation has indeed been performed successfully from normal coordinate force constants to Cartesian coordinate force constants.

| Mode | Ref. | Explicit | Re-diag |
|---|---|---|---|
| 1 | 3170.36 | 3170.354 | 3170.354 |
| 4(2) | 3137.34 | 3137.337 | 3137.337 |
| 2 | 3131.56 | 3131.562 | 3131.562 |
| 5(2) | 2583.82 | 2583.820 | 2583.820 |
| 6(2) | 2540.87 | 2540.869 | 2540.869 |
| 3 | 2388.12 | 2388.117 | 2388.117 |
| 5 + 7 | 2301.88 | 2301.874 | 2301.874 |
| 7 + 11 | 1734.36 | 1734.364 | 1734.364 |
| 4 | 1578.66 | 1578.660 | 1578.660 |
| 11(2) | 1433.93 | 1433.928 | 1433.928 |
| 12(2) | 1310.36 | 1310.360 | 1310.360 |
| 5 | 1293.31 | 1293.312 | 1293.312 |
| 6 | 1274.20 | 1274.198 | 1274.198 |
| 7 | 1015.48 | 1015.475 | 1015.475 |
| 8 | 1004.66 | 1004.658 | 1004.658 |
| 9 | 921.28 | 921.2834 | 921.2834 |
| 10 | 916.47 | 916.4719 | 916.4719 |
| 11 | 719.23 | 719.2262 | 719.2262 |
| 12 | 655.05 | 655.0473 | 655.0473 |

Table 2.2 The wavenumbers [$\mathrm{cm}^{-1}$] of the bands and resonances resulting from the second-order perturbation theory treatment of c-$C_3H_2D^+$ calculated using three different Cartesian force constants: Originally calculated (Ref. 77), converted from normal coordinate force constants using explicit regeneration method (this work), and converted from normal coordinate force constants using re-diagonalization method (this work).

## 2.7 Conclusions

It has been shown that the transformation from normal coordinates to Cartesian coordinates (and vice versa) can be made linear through the re-introduction of the translational and rotational eigenvectors. This method eliminates the need to calculate mixed derivatives as in the non-linear procedure. Two methods for regenerating these eigenvectors are presented, one from the re-diagonalization of the mass-weighted Hessian and one from a series of equations to explicitly reconstruct the missing rotational and translational eigenvectors. These two methods avoid the complicated non-linear transformation that that arises if the rotational and translational normal mode eigenvectors are neglected. Application of the two new approaches to the $H_2O$ and c-$C_3H_2D^+$ molecules has been performed to validate the equations and implementation.

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