

Vibrational isotope effect by the low rank perturbation method

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Received 14 November 2000

Mathematical formalism of the low rank perturbation method (LRP) is applied to the vibrational isotope effect in the harmonic approximation. A pair of two n -atom isotopic molecules A and B which are identical except for isotopic substitutions at ρ atomic sites is considered. Relations which express vibrational frequencies ω_k and normal modes Ψ_k of the perturbed isotopic molecule B in terms of the vibrational frequencies ν_i and normal modes Φ_i of the unperturbed molecule A are derived. In these relations complete specification of the unperturbed normal modes Φ_i is not required. Only amplitudes $\langle \tau | \Phi_i \rangle$ of normal modes Φ_i at sites τ affected by the isotopic substitution are needed.

KEY WORDS: low rank perturbation method, vibrational isotope effect, harmonic approximation

1. Introduction

The aim of this and the following paper is to provide a simple method for the calculation of the vibrational isotope effect in the harmonic approximation [1]. In this approximation one uses the classical model of the molecule where the nuclei are represented by mathematical points with masses. The displacement of nuclei from equilibrium positions can be described by Cartesian coordinates. If the molecule contains n nuclei, there are $3n$ such generic coordinates:

$$\xi_1, \xi_2, \dots, \xi_{3n}.$$

One can express the potential and the kinetic energy in terms of these coordinates. In the harmonic approximation [1] the potential energy is

$$V = \sum_{i < j} f_{ij} \xi_i \xi_j, \quad (1a)$$

where $f_{ij} = (\partial^2 V / \partial \xi_i \partial \xi_j)_0$ are force constants expressed in Cartesian coordinates.

Kinetic energy expressed in terms of Cartesian displacements from equilibria is

$$T = \frac{1}{2} \sum_i^{3n} m_i \left(\frac{d\xi_i}{dt} \right)^2. \quad (1b)$$

The solution of the above system consisting of n masses connected by harmonic forces leads to the generalised eigenvalue equation

$$\mathbf{F}|\Phi_i\rangle = \lambda_i \mathbf{M}|\Phi_i\rangle, \quad (2)$$

where \mathbf{F} is a $3n \times 3n$ force field matrix with matrix elements f_{ij} , while \mathbf{M} is a $3n \times 3n$ diagonal matrix which on a diagonal contains masses m_i . Eigenvalues λ_i of the eigenvalue equation (2) are related to the vibrational frequencies ν_i by

$$\lambda_i = 4\pi^2 \nu_i^2. \quad (2')$$

Without loss of generality one can assume eigenstates $|\Phi_i\rangle$ to be orthonormalized according to

$$\langle \Phi_i | \mathbf{M} | \Phi_j \rangle = \delta_{i,j}. \quad (3)$$

Instead of generic indices i and j we will use Greek letters α and β in order to label different atoms, and indices s and p in order to denote x -, y - and z -coordinates. Using this convention operators \mathbf{F} and \mathbf{M} can be written in the form

$$\mathbf{F} = \sum_{\alpha\beta}^n \sum_{sp}^3 f_{\alpha s, \beta p} |\alpha s\rangle \langle \beta p|, \quad \mathbf{M} = \sum_{\alpha}^n m_{\alpha} \sum_s^3 |\alpha s\rangle \langle \alpha s|, \quad (4)$$

where $|\alpha s\rangle$ is a ket vector, which denotes a unit displacement of α atom in the s th coordinate direction. These unit displacements are orthonormalized according to

$$\langle \alpha s | \beta p \rangle = \delta_{\alpha\beta} \delta_{sp} \quad (5a)$$

and they are complete:

$$\sum_{\alpha s} |\alpha s\rangle \langle \alpha s| = \mathbf{I}. \quad (5b)$$

We will also use explicit notation

$$|\alpha x\rangle \equiv |\alpha 1\rangle, \quad |\alpha y\rangle \equiv |\alpha 2\rangle, \quad |\alpha z\rangle \equiv |\alpha 3\rangle$$

in order to denote unit displacements of α atom in x -, y - and z -direction, respectively.

If in the original molecule some atoms are replaced by an isotope, to a very high degree of accuracy force field is not affected by those replacements [1]. In this approximation the perturbed equation describing isotopically substituted molecule is

$$\mathbf{F}|\Psi_k\rangle = \varepsilon_k (\mathbf{M} + \Delta\mathbf{M})|\Psi_k\rangle, \quad (6)$$

where $\Delta\mathbf{M}$ represents perturbation. We will label atoms that are affected by isotope substitution with Greek letters μ and τ . If there are ρ such atoms, perturbation $\Delta\mathbf{M}$ can be written in the form

$$\Delta\mathbf{M} = \sum_{\mu}^{\rho} \Delta m_{\mu} \sum_s^3 |\mu s\rangle \langle \mu s|, \quad (7)$$

where Δm_{μ} is isotope mass change of atom μ . Perturbed frequencies ω_k are related to the perturbed eigenvalues ε_k by

$$\varepsilon_k = 4\pi^2 \omega_k^2. \quad (6')$$

Eigenstates $|\Phi_i\rangle$ and $|\Psi_k\rangle$ have physical meaning of vibrations, and, therefore, we will use interchangeably both terms. When emphasis is on mathematics we will use term *eigenstates*, and when emphasis is on physics we will use term *vibrations*.

2. Multiple isotopic substitutions

One can solve perturbed eigenvalue equation (6) using the low rank perturbation (LRP) approach [2,3]. In this approach one expresses the eigenvalues and the eigenstates of the generalised perturbed eigenvalue equation in terms of the eigenvalues and eigenstates of the generalised unperturbed eigenvalue equation. One also makes a distinction between *cardinal* and *singular* eigenvalues and eigenstates of the perturbed equation. By definition, an eigenvalue ε_k of the perturbed equation is “cardinal” if it differs from all the eigenvalues λ_i of the unperturbed equation. Otherwise it is singular [2,3]. In other words, ε_k is cardinal if $\varepsilon_k \notin \{\lambda_i\}$ and singular if $\varepsilon_k \in \{\lambda_i\}$.

Concerning cardinal eigenvalues and eigenstates in appendix we prove the following theorem:

Theorem 1 (Cardinal eigenvalues and vibrations). Let (2) be the unperturbed isotope eigenvalue equation where $\nu_i = \sqrt{\lambda_i}/2\pi$ are the unperturbed frequencies. Let further the unperturbed vibrations be orthonormalized according to (3). Then:

- (a) $\varepsilon_k \notin \{\lambda_i\}$ is an eigenvalue of the perturbed isotope eigenvalue equation (6) if and only if it is a root of the equation

$$f(\varepsilon) \equiv \left| \mathbf{\Omega}(\varepsilon) + \frac{\Delta\mathbf{M}^{-1}}{\varepsilon} \right| = 0, \quad (8)$$

where $\mathbf{\Omega}$ is a $3\rho \times 3\rho$ Hermitian matrix with matrix elements

$$\mathbf{\Omega}_{\mu s, \tau p}(\varepsilon) = \mathbf{\Omega}_{\tau p, \mu s}^*(\varepsilon) = \sum_i^{3n} \frac{\langle \mu s | \Phi_i \rangle \langle \Phi_i | \tau p \rangle}{\varepsilon - \lambda_i}, \quad \mu, \tau = 1, \dots, \rho, \quad s, p = 1, 2, 3, \quad (9a)$$

while $\Delta\mathbf{M}^{-1}$ is $3\rho \times 3\rho$ diagonal matrix with matrix elements

$$\Delta\mathbf{M}_{\mu s, \tau p}^{-1} = \frac{\delta_{\mu\tau} \delta_{sp}}{\Delta m_\tau}. \quad (9b)$$

- (b) Let $\varepsilon_k \notin \{\lambda_i\}$ be the perturbed eigenvalue. Each vibration Ψ_k corresponding to this eigenvalue is of the form

$$|\Psi_k\rangle = \sum_i^{3n} \frac{\sum_\tau^\rho \sum_p^3 \langle \Phi_i | \tau p \rangle C_{\tau p}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle, \quad (10)$$

where the coefficients $C_{\tau p}$ are the components of a 3ρ column vector \mathbf{C} which is the (nontrivial) solution of the matrix equation

$$\left[\mathbf{\Omega}(\varepsilon_k) + \frac{\Delta\mathbf{M}^{-1}}{\varepsilon_k} \right] \mathbf{C} = 0. \quad (11)$$

In addition, coefficients $C_{\tau p}$ satisfy

$$C_{\tau p} = -\varepsilon_k \Delta m_\tau \langle \tau p | \Psi_k \rangle, \quad \tau = 1, \dots, \rho, \quad p = 1, 2, 3. \quad (12)$$

Conversely, if $\varepsilon_k \notin \{\lambda_i\}$ is the perturbed eigenvalue, each state Ψ_k of the form (10), where the coefficients $C_{\tau p}$ are the (nontrivial) solution of the linear set (11), is the corresponding vibration. Moreover, these coefficients satisfy (12).

Concerning degeneracy of the eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ one finds (see appendix):

Lemma 1. Let $\varepsilon_k \notin \{\lambda_i\}$ be a cardinal eigenvalue of the perturbed isotope equation (6). The degeneracy of this eigenvalue equals nullity of the matrix $\mathbf{\Omega}(\varepsilon_k) + \Delta\mathbf{M}^{-1}/\varepsilon_k$.

In other words, degeneracy of $\varepsilon_k \notin \{\lambda_i\}$ equals the number of linearly independent solutions \mathbf{C} to the matrix equation (11).

The above theorem gives a complete solution concerning cardinal $\varepsilon_k \notin \{\lambda_i\}$ eigenvalues and vibrations of the perturbed isotope equation (6). Given the unperturbed frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$ and unperturbed amplitudes $\langle \tau p | \Phi_i \rangle$, one obtains perturbed frequencies $\omega_k = \sqrt{\varepsilon_k}/2\pi$ and perturbed vibrations Ψ_k . First, one has to find the root or roots of the $3\rho \times 3\rho$ determinant $|\mathbf{\Omega}(\varepsilon) + \Delta\mathbf{M}^{-1}/\varepsilon|$. Each root $\varepsilon_k \notin \{\lambda_i\}$ of this determinant is an eigenvalue of (6). Once a particular eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ is found, and if the corresponding vibrations are required, one has to solve the homogenous set of 3ρ linear equations (11) in 3ρ unknowns $C_{\tau p}$. Linearly independent solutions \mathbf{C} to this equation generate linearly independent perturbed vibrations Ψ_k . In particular, each cardinal eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ of the perturbed eigenvalue equation is at most 3ρ -degenerate. This maximum possible degeneracy is achieved if and only if matrix $\mathbf{\Omega}(\varepsilon_k) + \Delta\mathbf{M}^{-1}/\varepsilon_k$ is a null matrix.

In a similar way one derives the following theorem, which gives the solution for the singular frequencies and vibrations.

Theorem 2 (Singular eigenvalues and vibrations). Assume the same conditions as in theorem 1. Let λ_j be a η -degenerate unperturbed eigenvalue, and denote the corresponding vibrations with $\Phi_{j\kappa}$ ($\kappa = 1, \dots, \eta$). Then:

- (a) $\varepsilon_k = \lambda_j$ is an eigenvalue of the perturbed eigenvalue equation (6) if and only if λ_j satisfies

$$f^0(\lambda_j) \equiv \begin{vmatrix} \mathbf{\Omega}^0(\lambda_j) + \Delta\mathbf{M}^{-1}/\lambda_j & \mathbf{W}/\lambda_j \\ \mathbf{W}^T/\lambda_j & \mathbf{0}_\eta \end{vmatrix} = 0, \quad (13)$$

where $\mathbf{\Omega}^0(\varepsilon)$ is a $3\rho \times 3\rho$ Hermitian matrix with matrix elements

$$\mathbf{\Omega}_{\mu s, \tau p}^0(\varepsilon) = \sum_{i(\lambda_i \neq \lambda_j)}^{3n} \frac{\langle \mu s | \Phi_i \rangle \langle \Phi_i | \tau p \rangle}{\varepsilon - \lambda_i}, \quad (14a)$$

\mathbf{W} is a $3\rho \times \eta$ matrix with matrix elements

$$\mathbf{W}_{\mu s, \kappa} = -\frac{\langle \mu s | \Phi_{j\kappa} \rangle}{\Delta m_\mu}, \quad \mu = 1, \dots, \rho, \quad s = 1, 2, 3, \quad \kappa = 1, \dots, \eta, \quad (14b)$$

$\Delta\mathbf{M}^{-1}$ is a diagonal matrix with matrix elements (9b), and $\mathbf{0}_\eta$ is a $\eta \times \eta$ null matrix.

- (b) Let $\varepsilon_k = \lambda_j$ be the perturbed eigenvalue. Each vibration Ψ_k corresponding to this eigenvalue is of the form

$$|\Psi_k\rangle = \sum_{i(\lambda_i \neq \lambda_j)}^{3n} \frac{\sum_\tau \sum_p \langle \Phi_i | \tau p \rangle C_{\tau p}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle + \sum_\kappa D_\kappa |\Phi_{j\kappa}\rangle, \quad (15)$$

where the coefficients $C_{\tau p}$ and D_κ form a $(3\rho + \eta)$ column vector which is the (nontrivial) solution of the matrix equation

$$\begin{bmatrix} \mathbf{\Omega}^0(\lambda_j) + \Delta\mathbf{M}^{-1}/\lambda_j & \mathbf{W}/\lambda_j \\ \mathbf{W}^T/\lambda_j & \mathbf{0}_\eta \end{bmatrix} \begin{bmatrix} \mathbf{C} \\ \mathbf{D} \end{bmatrix} = 0. \quad (16)$$

In addition, these coefficients satisfy

$$C_{\tau p} = -\varepsilon_k \Delta m_\tau \langle \tau p | \Psi_k \rangle, \quad D_\kappa = \langle \Phi_{j\kappa} | \mathbf{M} | \Psi_k \rangle, \\ \tau = 1, \dots, \rho, \quad p = 1, 2, 3, \quad \kappa = 1, \dots, \eta. \quad (17)$$

Conversely, if ε_k is a singular eigenvalue of (6), each state Ψ_k of the form (15), where the coefficients $C_{\tau p}$ and D_κ are the (nontrivial) solution of the linear set (16), is the corresponding vibration.

Concerning degeneracy of singular eigenvalues one finds in analogy to lemma 1:

Lemma 2. Let $\varepsilon_k = \lambda_j$ be a singular eigenvalue of the perturbed isotope equation (6). The degeneracy of this eigenvalue equals the number of linearly independent solutions $[\mathbf{C}, \mathbf{D}]$ to the matrix equation (16).

In particular, if the unperturbed eigenvalue λ_j is η -degenerate, perturbed eigenvalue $\varepsilon_k = \lambda_j$ is at most $(3\rho + \eta)$ -degenerate. Also, if $\eta > 3\rho$, perturbed eigenvalue $\varepsilon_k = \lambda_j$ is at least $(\eta - 3\rho)$ -degenerate.

In order to analyse in more detail singular solutions given by theorem 2, it is convenient to distinguish *active* and *passive* unperturbed eigenvalues [2,3]. The notion of active and passive eigenvalues is defined relative to the perturbation $\Delta\mathbf{M}$.

If the perturbation $\Delta\mathbf{M}$ satisfies

$$\Delta\mathbf{M}|\Phi_{j\kappa}\rangle = 0, \quad \kappa = 1, \dots, \eta, \quad (18a)$$

the eigenvalue λ_j is *passive*, otherwise it is *active*. Thus, the eigenvalue λ_j is passive if the invariant subspace associated with this eigenvalue is contained in a null subspace of the operator $\Delta\mathbf{M}$.

Requirement (18a) is equivalent to

$$\langle \mu s | \Phi_{j\kappa} \rangle = 0, \quad \mu = 1, \dots, \rho, \quad s = 1, 2, 3, \quad \kappa = 1, \dots, \eta. \quad (18b)$$

Physically, if the frequency $\nu_j = \sqrt{\lambda_j}/2\pi$ is passive, all the corresponding unperturbed vibrations $\Phi_{j\kappa}$ have amplitudes zero at each atom which is substituted by an isotope. Such a vibration can not be affected by the isotopic substitutions. Hence, if the unperturbed eigenvalue λ_j is passive, this eigenvalue is also an eigenvalue of the perturbed system, and the unperturbed vibrations $\Phi_{j\kappa}$ are also vibrations of the perturbed system.

One derives the same conclusion from the above theorem. In general, matrix $\mathbf{\Omega}(\varepsilon)$ is singular in the point $\varepsilon = \lambda_j$. However, if the eigenvalue λ_j is passive, matrix $\mathbf{\Omega}(\varepsilon)$ is regular in this point, and moreover, one finds $\mathbf{\Omega}(\varepsilon) \equiv \mathbf{\Omega}^0(\varepsilon)$. In addition, if λ_j is passive, matrix \mathbf{W} vanishes, i.e., $\mathbf{W} = \mathbf{0}$. Hence, matrix equation (16) reduces to

$$\left[\mathbf{\Omega}(\lambda_j) + \frac{\Delta\mathbf{M}^{-1}}{\lambda_j} \right] \mathbf{C} = 0. \quad (16a)$$

Since there is no condition on the coefficients D_κ , these coefficients are arbitrary. Hence, there are always η solutions with $\mathbf{C} = 0$ and with different coefficients D_κ nonzero. According to (15), the corresponding perturbed vibrations coincide with unperturbed vibrations $\Phi_{j\kappa}$. Thus, if λ_j is passive, it is a singular eigenvalue of the perturbed equation, and each unperturbed vibration $\Phi_{j\kappa}$ is also perturbed vibration.

In addition to the solutions with $\mathbf{C} = 0$ which always exist if λ_j is passive, relation (16a) can also have a nontrivial solution. Those additional solutions can be chosen to satisfy $\mathbf{D} = 0$. Further, relation (16a) is equivalent to the relation (11) with $\varepsilon_k = \lambda_j$. Also with $\mathbf{D} = 0$ eigenstate (15) reduces to the eigenstate (10). Thus, all such extra solutions can be obtained from relations (8), (10) and (11). In conclusion, each solution to (8), not only cardinal solutions of the type $\varepsilon_k \notin \{\lambda_i\}$, is an eigenvalue of the perturbed system. The set of all solutions to (8) contains all cardinal eigenvalues, and in addition it may contain some singular eigenvalues. The corresponding eigenstates are

given by (10). All the remaining singular eigenstates are the same as the corresponding unperturbed eigenstates.

The point of the above discussion is that the application of theorem 2 is nontrivial only for these singular solutions for which λ_j is active. If λ_j is passive and η -degenerate, $\varepsilon_k = \lambda_j$ is at least η -degenerate eigenvalue of the perturbed system. There are always η perturbed vibrations that coincide with η unperturbed vibrations $\Phi_{j\kappa}$. If there are any remaining vibrations, these vibrations are all of the form (10), i.e., they can be obtained by applying theorem 1. Thus, theorem 2 should be explicitly utilised only in order to obtain genuine singular solutions, that is, in the case when λ_j is active.

According to the above analysis, passive eigenvalues λ_j and the corresponding eigenstates $\Phi_{j\kappa}$ are not affected by the isotopic substitution. Another point to emphasise is that passive eigenvalues and eigenstates do not enter any of the relations (8)–(11). Hence, perturbed cardinal solutions do not depend in any way on the unperturbed passive solutions.

The above two theorems, in conjuncture with lemmas 1 and 2 give a complete solution to the vibrational isotope effect in the harmonic approximation. In order to obtain perturbed frequencies and vibrations by this method, no information about force constants is required. According to relations (8), (9), (13) and (14) perturbed frequencies depend only on the unperturbed frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$, on the isotope mass changes Δm_τ at atoms τ that are substituted by an isotope, and on the unperturbed amplitudes $\langle \tau s | \Phi_i \rangle$ at those atoms. No knowledge of the amplitudes $\langle \alpha s | \Phi_i \rangle$ of the vibrations Φ_i at atoms α that are not substituted by an isotope is required. This shows that perturbed frequencies do not depend on any fine details of a molecule outside the region affected by the isotopic substitutions. In particular, those frequencies do not depend in any direct way on atomic masses and force constants outside this region. All the potentially huge information about the molecular structure outside this region is succinctly concentrated into the global information about unperturbed frequencies.

The same is true for the perturbed vibrations. According to relations (10) and (15) each perturbed vibration Ψ_k is expressed as a linear combination $\Psi_k = \sum_i a_i |\Phi_i\rangle$ of unperturbed vibrations Φ_i . Expansion coefficients a_i depend only on the unperturbed frequencies ν_i , on the isotope mass changes Δm_τ , and on the unperturbed amplitudes $\langle \tau s | \Phi_i \rangle$ at atoms τ that are affected by the isotopic substitution. In this sense perturbed vibrations Ψ_k depend exactly on the same quantities as perturbed frequencies ω_k . In particular, if one knows matrix elements $\langle \Phi_i | \mathbf{O} | \Phi_j \rangle$ of some observable \mathbf{O} between unperturbed vibrations Φ_i , using these relations one obtains matrix elements $\langle \Psi_k | \mathbf{O} | \Psi_l \rangle$ of this observable between any two perturbed vibrations Ψ_k and Ψ_l . For example, from the known transition probability amplitudes between unperturbed vibrations one obtains in this way transition probability amplitudes between perturbed vibrations, etc. However, if the amplitudes of the perturbed vibrations are required, the above relations produce only amplitudes $\langle \tau s | \Psi_k \rangle$ at the positions of atoms τ that are substituted by an isotope. Namely, if $\Psi_k = \sum_i a_i |\Phi_i\rangle$ then $\langle \tau s | \Psi_k \rangle = \sum_i a_i \langle \tau s | \Phi_i \rangle$, and since coefficients a_i and unperturbed amplitudes $\langle \tau s | \Phi_i \rangle$ are known, perturbed amplitude $\langle \tau s | \Psi_k \rangle$ is also known. If perturbed amplitude $\langle \alpha s | \Psi_k \rangle$ at some atom α that is not affected by the isotopic sub-

stitution is required, one has to know (in addition to the above unperturbed quantities) unperturbed amplitudes $\langle \alpha s | \Phi_i \rangle$ at the position of this atom.

3. Orthonormalization of unperturbed vibrations and nonproper vibrations

Consider now the question of the orthonormality of the unperturbed vibrations. Relations given in the above two theorems are valid provided the unperturbed vibrations Φ_i are orthonormalized according to (3). If two unperturbed vibrations have different frequencies, they are automatically orthogonal to each other, and one has only to normalise these vibrations, which is trivial. The problem is more complex if some unperturbed vibrations are degenerate, since degenerate vibrations are not automatically orthogonal to each other, and one has to choose such a linear combination of degenerate vibrations, which satisfy orthogonality relation (3). In general, we do not know in advance which vibrations will be degenerate, and this depends on a particular problem. However, there are always six (in the case of nonlinear molecules) or five (in the case of linear molecules) nonproper vibrations which are degenerate and which correspond to the frequency $\nu_0 = 0$. These nonproper vibrations correspond to three translations and three (two) rotations, and since they are always present, they can be treated explicitly.

Denote the three nonproper vibrations which correspond to translation in the x -, y - and z -direction with Φ_{Tx} , Φ_{Ty} and Φ_{Tz} , respectively. Similarly, denote the three nonproper vibrations which correspond to rotations around x -, y - and z -axis with Φ_{Rx} , Φ_{Ry} and Φ_{Rz} , respectively. One can show that normalised nonproper vibrations Φ_{Ts} and Φ_{Rs} are (see appendix):

$$|\Phi_{Tx}\rangle = \frac{1}{\sqrt{M}} \sum_{\alpha}^n |\alpha x\rangle,$$

$$|\Phi_{Ty}\rangle = \frac{1}{\sqrt{M}} \sum_{\alpha}^n |\alpha y\rangle, \quad (19a)$$

$$|\Phi_{Tz}\rangle = \frac{1}{\sqrt{M}} \sum_{\alpha}^n |\alpha z\rangle,$$

$$|\Phi_{Rx}\rangle = \frac{1}{\sqrt{I_x}} \sum_{\alpha}^n [y_{\alpha} |\alpha z\rangle - z_{\alpha} |\alpha y\rangle],$$

$$|\Phi_{Ry}\rangle = \frac{1}{\sqrt{I_y}} \sum_{\alpha}^n [z_{\alpha} |\alpha x\rangle - x_{\alpha} |\alpha z\rangle], \quad (19b)$$

$$|\Phi_{Rz}\rangle = \frac{1}{\sqrt{I_z}} \sum_{\alpha}^n [x_{\alpha} |\alpha y\rangle - y_{\alpha} |\alpha x\rangle],$$

where $M = \sum_{\alpha} m_{\alpha}$ is a total molecular mass, I_x , I_y and I_z are molecular moments of inertia, and x_{α} , y_{α} and z_{α} are x -, y - and z -coordinates of atom α , respectively.

The problem of mutual orthogonality of the nonproper vibrations (19) is addressed by the following lemma proven in the appendix:

Lemma 3. Let the coordinate system be chosen in such a way that the coordinate origin is situated in the centre of mass of the unperturbed molecule, and that coordinate axis coincide with the principal axis of this molecule. Then the nonproper vibrations (19) satisfy orthonormality relations (3).

In what follows we will assume that besides translations and rotations there are no other nonproper vibrations. In other words, there are no such modes as free rotation around some molecular axis, etc. If this is not the case, one has to orthogonalize all such nonproper vibrations explicitly with nonproper vibrations (19).

Since all proper vibrations Φ_i have nonzero frequency, they are automatically orthogonal to nonproper vibrations (19):

$$\begin{aligned} \langle \Phi_{T_x} | \mathbf{M} | \Phi_i \rangle &= \langle \Phi_{T_y} | \mathbf{M} | \Phi_i \rangle = \langle \Phi_{T_z} | \mathbf{M} | \Phi_i \rangle = 0, \\ \langle \Phi_{R_x} | \mathbf{M} | \Phi_i \rangle &= \langle \Phi_{R_y} | \mathbf{M} | \Phi_i \rangle = \langle \Phi_{R_z} | \mathbf{M} | \Phi_i \rangle = 0. \end{aligned} \quad (20)$$

These relations express the requirement that during molecular vibration the centre of mass is not displaced, and that no vibration contains any component of angular momentum. For example, one has explicitly

$$\langle \Phi_{T_x} | \mathbf{M} | \Phi_i \rangle = \sum_{\alpha}^n m_{\alpha} \langle \alpha x | \Phi_i \rangle = 0$$

and

$$\langle \Phi_{R_z} | \mathbf{M} | \Phi_i \rangle = \sum_{\alpha}^n m_{\alpha} [x_{\alpha} \langle \alpha y | \Phi_i \rangle - y_{\alpha} \langle \alpha x | \Phi_i \rangle] = 0.$$

The first expression tells that x -component of the molecular centre of mass is not displaced during molecular vibration Φ_i , and the second expression tells that during this vibration there is no rotation around z -axis.

Using (19) the expression (10) for the perturbed vibration can be written as

$$|\Psi_k\rangle = \frac{1}{\varepsilon_k} \left[\sum_s^3 T_s |\Phi_{T_s}\rangle + \sum_s^3 R_s |\Phi_{R_s}\rangle \right] + \sum_i^{3n-6} \frac{\sum_{\tau}^{\rho} \sum_s^3 \langle \Phi_i | \tau s \rangle C_{\tau s}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle, \quad (21a)$$

where coefficients T_s and R_s are

$$\begin{aligned} T_s &= \frac{1}{\sqrt{M}} \sum_{\tau}^{\rho} C_{\tau s}, \\ R_x &= \frac{1}{\sqrt{I_x}} \sum_{\tau}^{\rho} [y_{\tau} C_{\tau z} - z_{\tau} C_{\tau y}], \end{aligned} \quad (21b)$$

and analogously for the coefficients R_y and R_z .

In a similar way, one eliminates nonproper vibrations from the expression (9a):

$$\Omega_{\mu x, \tau x}(\varepsilon) = \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{y_\mu y_\tau}{I_z} + \frac{z_\mu z_\tau}{I_y} \right] + \sum_i^{3n-6} \frac{\langle \mu x | \Phi_i \rangle \langle \Phi_i | \tau x \rangle}{\varepsilon - \lambda_i}, \quad (22a)$$

$$\Omega_{\mu x, \tau y}(\varepsilon) = -\frac{x_\tau y_\mu}{\varepsilon I_z} + \sum_i^{3n-6} \frac{\langle \mu x | \Phi_i \rangle \langle \Phi_i | \tau y \rangle}{\varepsilon - \lambda_i}. \quad (22b)$$

Remaining matrix elements $\Omega_{\mu y, \tau y} = \Omega_{\tau y, \mu y}^*$, $\Omega_{\mu z, \tau z} = \Omega_{\tau z, \mu z}^*$, $\Omega_{\mu y, \tau z} = \Omega_{\tau z, \mu y}^*$ and $\Omega_{\mu z, \tau x} = \Omega_{\tau x, \mu z}^*$ are obtained by a cyclic substitution in (22a) and (22b).

In the case of nonlinear molecules the summation over i in relations (21) and (22) is performed over $(3n-6)$ proper vibrations, while the contribution of nonproper vibrations is taken into account by the first terms in those relations. In the case of linear molecules, each term containing moment of inertia $I_x = 0$ along the molecular axis should be omitted, and summation is performed over $(3n-5)$ proper vibrations.

Similar explicit relations are obtained in the case of singular solutions, which we omit here for the sake of simplicity.

4. Orthonormalization of perturbed vibrations

In analogy to (3), perturbed vibrations can be orthonormalized according to

$$\langle \Psi_k | \mathbf{M} + \Delta \mathbf{M} | \Psi_l \rangle = \delta_{kl}. \quad (23)$$

Vibrations belonging to different frequencies are automatically orthogonal to each other. In particular, each proper vibration Ψ_k is orthogonal to perturbed nonproper vibrations $|\Psi_{Ts}\rangle$ and $|\Psi_{Rs}\rangle$:

$$\langle \Psi_{Ts} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle = 0, \quad \langle \Psi_{Rs} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle = 0, \quad s = 1, 2, 3. \quad (23a)$$

Relations (23a) follow from the general form of relations (6). However, it is instructive to give an independent derivation of those relations. This provides an independent verification of the validity of the LRP approach.

Perturbed molecule has in general different centre of mass and different principal axes from the unperturbed molecule. Hence, perturbed nonproper vibrations $|\Psi_{Ts}\rangle$ and $|\Psi_{Rs}\rangle$ usually differ from unperturbed nonproper vibrations $|\Phi_{Ts}\rangle$ and $|\Phi_{Rs}\rangle$. However, since the perturbed and the unperturbed molecule have the same geometry, each translation and each rotation of the perturbed molecule is a linear combination of translations and rotations of the unperturbed molecule. Conditions (23a) are, hence, equivalent to the conditions

$$\langle \Phi_{Ts} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle = 0, \quad \langle \Phi_{Rs} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle = 0, \quad s = 1, 2, 3. \quad (23b)$$

Assume that perturbed vibration Ψ_k is cardinal, and consider the first relation in (23b). Inserting expression (10) for the cardinal vibration Ψ_k into this relation one finds

$$\begin{aligned} & \langle \Phi_{Ts} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle \\ &= \sum_i^{3n} \frac{\sum_\tau^\rho \sum_p^3 \langle \Phi_i | \tau p \rangle C_{\tau p}}{\varepsilon_k - \lambda_i} \langle \Phi_{Ts} | \mathbf{M} | \Phi_i \rangle + \sum_i^{3n} \frac{\sum_\tau^\rho \sum_p^3 \langle \Phi_i | \tau p \rangle C_{\tau p}}{\varepsilon_k - \lambda_i} \langle \Phi_{Ts} | \Delta \mathbf{M} | \Phi_i \rangle. \end{aligned} \quad (24)$$

Due to (3), all terms in the first sum of (24) vanish, except for the term involving $\Phi_i = \Phi_{Ts}$. Further, from (19a) and (7)

$$\langle \Phi_{Ts} | \Delta \mathbf{M} | \Phi_i \rangle = \frac{1}{\sqrt{M}} \sum_\tau^\rho \Delta m_\tau \langle \tau s | \Phi_i \rangle.$$

Hence, the right-hand side of (24) equals

$$\frac{1}{\varepsilon_k} \sum_\tau^\rho \sum_p^3 \langle \Phi_{Ts} | \tau p \rangle C_{\tau p} + \frac{1}{\sqrt{M}} \sum_\mu^\rho \left[\sum_\tau^\rho \sum_p^3 \boldsymbol{\Omega}_{\mu s, \tau p}(\varepsilon_k) C_{\tau p} \right] \Delta m_\mu.$$

However, according to (11) the quantity in the brackets equals $[\boldsymbol{\Omega}(\varepsilon_k) \mathbf{C}]_{\mu s} = -C_{\mu s} / \varepsilon_k \Delta m_\mu$, while (19a) implies $\langle \Phi_{Ts} | \tau p \rangle = \delta_{sp} / \sqrt{M}$. One thus finally obtains $\langle \Phi_{Ts} | \mathbf{M} + \Delta \mathbf{M} | \Psi \rangle = 0$. This shows that each perturbed vibration (10) is orthogonal to the unperturbed translation Φ_{Ts} .

Consider now unperturbed rotations Φ_{Rx} , for example, a rotation Φ_{Rx} . From (19b) and (7) one obtains

$$\langle \Phi_{Rx} | \Delta \mathbf{M} | \Phi_i \rangle = \frac{1}{\sqrt{I_x}} \sum_\tau^\rho \Delta m_\tau [y_\tau \langle \tau z | \Phi_i \rangle - z_\tau \langle \tau y | \Phi_i \rangle].$$

Hence, one finds that the expression $\langle \Phi_{Rx} | \mathbf{M} + \Delta \mathbf{M} | \Psi_k \rangle$ equals

$$\begin{aligned} & \frac{1}{\varepsilon_k} \sum_\tau^\rho \sum_p^3 \langle \Phi_{Rx} | \tau p \rangle C_{\tau p} \\ &+ \frac{1}{\sqrt{I_x}} \sum_\mu^\rho \left[y_\mu \sum_\tau^\rho \sum_p^3 \boldsymbol{\Omega}_{\mu z, \tau p}(\varepsilon_k) C_{\tau p} - z_\mu \sum_\tau^\rho \sum_p^3 \boldsymbol{\Omega}_{\mu y, \tau p}(\varepsilon_k) C_{\tau p} \right] \Delta m_\mu. \end{aligned}$$

According to (11) the quantity in the brackets equals $(z_\mu C_{\mu y} - y_\mu C_{\mu z}) / \varepsilon_k \Delta m_\mu$, while according to (19b) one has $\langle \Phi_{Rx} | \tau p \rangle = (y_\tau \delta_{zp} - z_\tau \delta_{yp}) / \sqrt{I_x}$. Inserting into the above expression one obtains $\langle \Phi_{Rx} | \mathbf{M} + \Delta \mathbf{M} | \Psi \rangle = 0$.

Since perturbed translations and rotations are linear combinations of unperturbed translations and rotations, this proves (23a) in the case when Ψ_k is a cardinal vibration (10). Analogous results are obtained for singular vibrations (15).

Perturbed vibrations (10) and (15) are not orthonormalized, and hence, these vibrations in general do not satisfy (23). However, if the orthonormalization is required, it can be easily done. If the perturbed vibration Ψ_k is nondegenerate, it is automatically orthogonal to all other perturbed vibrations, and hence, one has only to normalize this vibration. The problem of mutual orthogonality of the perturbed vibrations can appear only for degenerate vibrations.

If Ψ_k and Ψ_l are two (not necessarily distinct) perturbed vibrations, they can be written as linear combinations $\Psi_k = \sum_i c_i \Phi_i$ and $\Psi_l = \sum_i d_i \Phi_i$, where coefficients c_i and d_i are determined by relations (10) and/or (15). Hence,

$$\langle \Psi_k | \mathbf{M} + \Delta \mathbf{M} | \Psi_l \rangle = \sum_i^{3n} c_i^* d_i + \sum_{i,j}^{3n} c_i^* d_j \langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle. \quad (25a)$$

Thus, the orthonormalization of perturbed vibrations requires calculation of matrix elements $\langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle$. Using (7) those matrix elements can be expressed in terms of amplitudes $\langle \mu s | \Phi_i \rangle$:

$$\langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle = \sum_{\mu}^{\rho} \Delta m_{\mu} \sum_s^3 \langle \Phi_i | \mu s \rangle \langle \mu s | \Phi_j \rangle. \quad (25b)$$

This shows that in order to orthonormalize perturbed vibrations, only the amplitudes $\langle \mu s | \Phi_i \rangle$ of the unperturbed vibrations Φ_i at atomic sites μ that are affected by the isotopic substitutions are required. No knowledge of the amplitudes of the unperturbed vibrations Φ_i at the remaining part of a molecule is needed.

In conclusion, one can normalize perturbed vibrations, which usually extend over entire molecule, without any detailed knowledge about the molecular structure (force constants, atomic masses, atomic positions etc.) outside the region affected by the isotopic substitutions.

5. Single isotope substitution

Consider two molecules A and B_{τ} which are identical except for a single isotopic substitution at atomic site τ . In this case perturbation (7) reduces to

$$\Delta \mathbf{M} = \Delta m_{\tau} \sum_s^3 |\tau s\rangle \langle \tau s|.$$

Here Δm_{τ} is the isotope mass change of the atom τ , while $|\tau s\rangle$ is a unit displacement of this atom in the s th coordinate direction.

Applying theorem 1 to this case, one finds that $\varepsilon_k \notin \{\lambda_i\}$ is an eigenvalue of the perturbed isotope equation if and only if it is a root of the function $f(\varepsilon)$

$$f(\varepsilon) \equiv \left| \mathbf{\Omega}(\varepsilon) + \frac{\mathbf{I}_3}{\varepsilon \Delta m_{\tau}} \right| = 0, \quad (26)$$

where $\mathbf{\Omega}(\varepsilon)$ is a 3×3 matrix with matrix elements

$$\mathbf{\Omega}_{sp}(\varepsilon) = \sum_i^{3n} \frac{\langle \tau s | \Phi_i \rangle \langle \Phi_i | \tau p \rangle}{\varepsilon - \lambda_i} \quad (27)$$

and where \mathbf{I}_3 is a unit 3×3 matrix.

If one eliminates nonproper vibrations according to (22), matrix elements of a matrix $\mathbf{\Omega}$ can be written in a more explicit form

$$\mathbf{\Omega}_{xx}(\varepsilon) = \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{y_\tau^2}{I_z} + \frac{z_\tau^2}{I_y} \right] + \sum_i^{3n-6} \frac{\langle \tau x | \Phi_i \rangle \langle \Phi_i | \tau x \rangle}{\varepsilon - \lambda_i}, \quad (28a)$$

$$\mathbf{\Omega}_{xy}(\varepsilon) = \mathbf{\Omega}_{yx}^*(\varepsilon) = -\frac{x_\tau y_\tau}{\varepsilon I_z} + \sum_i^{3n-6} \frac{\langle \tau x | \Phi_i \rangle \langle \Phi_i | \tau y \rangle}{\varepsilon - \lambda_i}. \quad (28b)$$

Cyclically one obtains remaining matrix elements $\mathbf{\Omega}_{yy}(\varepsilon)$, $\mathbf{\Omega}_{zz}(\varepsilon)$, $\mathbf{\Omega}_{xz}(\varepsilon) = \mathbf{\Omega}_{zx}^*(\varepsilon)$ and $\mathbf{\Omega}_{yz}(\varepsilon) = \mathbf{\Omega}_{zy}^*(\varepsilon)$.

Further, if $\varepsilon_k \notin \{\lambda_i\}$ is a perturbed eigenvalue, each state of the form

$$|\Psi_k\rangle = \sum_j \frac{\sum_s \langle \Phi_j | \tau s \rangle C_s}{\varepsilon_k - \lambda_j} |\Phi_j\rangle, \quad (29)$$

where coefficients C_s are components of a column vector \mathbf{C} which is the (nontrivial) solution of

$$\left[\mathbf{\Omega}(\varepsilon_k) + \frac{\mathbf{I}_3}{\varepsilon_k \Delta m_\tau} \right] \mathbf{C} = 0, \quad (30)$$

is a perturbed vibration corresponding to this eigenvalue. In addition, coefficients C_s satisfy

$$C_s = -\varepsilon_k \Delta m_\tau \langle \tau s | \Psi_k \rangle. \quad (31)$$

Perturbed vibration (29) can be written in a more explicit form

$$|\Psi_k\rangle = \frac{1}{\varepsilon_k} \left[\sum_s^3 T_s |\Phi_{Ts}\rangle + \sum_s^3 R_s |\Phi_{Rs}\rangle \right] + \sum_j \frac{\sum_s^3 \langle \Phi_j | \tau s \rangle C_s}{\varepsilon_k - \lambda_j} |\Phi_j\rangle, \quad (32a)$$

where

$$T_s = \frac{C_s}{\sqrt{M}}, \quad R_1 \equiv R_x = \frac{y_\tau C_z - z_\tau C_y}{\sqrt{I_x}}, \quad (32b)$$

and cyclically for coefficients R_2 and R_3 . Each perturbed proper vibration Ψ_k is, thus, a linear combination of unperturbed nonproper vibrations (translations and rotations) Φ_{Ts} and Φ_{Rs} and unperturbed proper vibrations Φ_j . Translations and rotations Φ_{Ts} and Φ_{Rs} compensate for the recoil introduced by the isotope mass change Δm_τ .

The above relations are valid for cardinal solutions, and they apply directly to non-linear molecules. In the case of linear molecules, each term containing moment of inertia $I_x = 0$ should be omitted, and the summation is performed over $(3n - 5)$ proper vibrations.

Similar relations are obtained for singular solutions.

6. Conclusions

The above two theorems, in conjuncture with lemmas 1–3 and explicit relations (21) and (22), give a complete solution to the vibrational isotope effect in the harmonic approximation. The obtained relations produce all perturbed frequencies and all the corresponding vibrations.

In order to obtain perturbed frequencies and vibrations, no information about force constants is required. These perturbed quantities depend only on the unperturbed frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$, on the changes Δm_τ of the masses of atoms τ that are substituted by an isotope, and on the amplitudes $\langle \tau s | \Phi_i \rangle$ of the unperturbed vibrations Φ_i at the positions of these atoms. No information on the amplitudes $\langle \alpha s | \Phi_i \rangle$ of the vibrations Φ_i at atoms α that are not substituted by an isotope is required. This applies in particular to the normalization of the perturbed vibrations. In conclusion, perturbed frequencies and vibrations do not depend on the unperturbed amplitudes at any atom which is not replaced by an isotope. This is a remarkable result. Conceptually it shows that the perturbed frequencies and vibrations do not depend on any fine details of molecular structure outside the region affected by the perturbation. All information due to the molecular region unaffected by the perturbation $\Delta \mathbf{M}$ is condensed in the global information about unperturbed frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$. In addition, the information about the unperturbed amplitudes $\langle \tau s | \Phi_{T_s} \rangle$ and $\langle \tau s | \Phi_{R_s} \rangle$ of the nonproper vibrations Φ_{T_s} and Φ_{R_s} can be replaced by the information about the coordinate positions (x_τ, y_τ, z_τ) of those atoms that are substituted by an isotope, and by four global characteristics: total molecular mass M of the unperturbed molecule, and three principal moments of inertia I_x , I_y and I_z of this molecule.

Though the obtained LRP relations express each perturbed vibration $|\Psi_k\rangle$ as a linear combination of unperturbed vibrations Φ_i , those relations do not explicitly specify amplitudes $\langle \alpha s | \Psi_k \rangle$ of the perturbed vibrations $|\Psi_k\rangle$ at those atoms that are not substituted by an isotope. However, if one knows matrix elements $\langle \Phi_i | \mathbf{O} | \Phi_j \rangle$ of an observable \mathbf{O} between the unperturbed vibrations $|\Phi_i\rangle$, then those relations produce matrix elements $\langle \Psi_k | \mathbf{O} | \Psi_l \rangle$ of this observable between any two perturbed vibrations. This is usually all what is required, and in this sense the obtained LRP relations provide a sufficiently complete specification of all perturbed vibrations.

In general, it is not important how frequencies ν_i and unperturbed amplitudes $\langle \tau s | \Phi_i \rangle$ were obtained. These quantities can be obtained by solving the unperturbed eigenvalue equation (2) with some assumed force field, in a standard way. However, these quantities can be also obtained in many other ways. For example, one can use experimental data for the unperturbed frequencies. Concerning unperturbed amplitudes,

in some cases these amplitudes can be obtained from the molecular symmetry alone [4]. In the case of linear and out-of-plane vibrations of planar molecules these amplitudes can be obtained from the experimental frequencies of selected monosubstituted isotopomers [5], etc. In this later case the entire information about the unperturbed system is completely reduced to the experimental data: frequencies of the unperturbed molecule, and frequencies of few selected monosubstituted molecules.

An additional point to emphasise is that the information required to solve the perturbed problem by the LRP method is relatively small. In order to find all perturbed frequencies and vibrations one has to know $(3n - 6)$ unperturbed vibrations ν_i , $3\rho(3n - 6)$ unperturbed amplitudes $\langle \mu_s | \Phi_i \rangle$, ρ mass differences Δm_τ , the total molecular mass M , and the three moments of inertia along principal axis. This totals to approximately $9\rho n$ quantities. If $\rho \ll n$, which is usually the case, this is substantially less than approximately $9n^2/2$ force constants. Thus, the LRP approach requires much less data, than the standard approach with force constants. Of course, in a standard approach one can use various models which utilise reduced number of force constants [1]. Those models are based on some plausible assumptions, such as the assumption of central forces, the assumption of valence forces, and alike [1]. However, due to neglect of some force constants, all such models are only approximate, while the suggested LRP approach is in the harmonic approximation exact.

Finally and not the least important, one finds that the operation count for the solution of the LRP equations is of the order $O(n^2)$, while operation count for the solution of the perturbed equation (6) in a standard way is usually of the order $O(n^3)$ [2,3]. Thus, in the case of large molecules (big n), LRP approach is numerically much faster than the standard approach.

Appendix

A.1. Proof of theorems 1 and 2

One can show that theorems 1 and 2 are a special case of much more general low rank perturbation (LRP) theorems [2,3]. However, we prefer to give here an independent derivation of these theorems. This is less time consuming than to cite general LRP theorems, and in addition, it has the advantage of illustrating the spirit of the LRP approach.

Multiplying relation (6) from left by $\langle \Phi_i |$ and using (2) one obtains

$$(\varepsilon_k - \lambda_i) \langle \Phi_i | \mathbf{M} | \Psi_k \rangle = -\varepsilon_k \langle \Phi_i | \Delta \mathbf{M} | \Psi_k \rangle. \quad (\text{A.1})$$

Also from relation (3) one finds

$$\mathbf{I} = \sum_i^{3n} |\Phi_i\rangle \langle \Phi_i| \mathbf{M}, \quad (\text{A.2})$$

where \mathbf{I} is a unit operator.

Relation (A.1) is our starting relation for the derivation of theorems 1 and 2. Consider, first, theorem 1.

Let $\varepsilon_k \notin \{\lambda_i\}$. Dividing both sides of (A.1) by $(\varepsilon_k - \lambda_i)$, multiplying from left by $|\Phi_i\rangle$, summing over i and using (A.2) one obtains

$$|\Psi_k\rangle = -\varepsilon_k \sum_i \frac{\langle \Phi_i | \Delta \mathbf{M} | \Psi_k \rangle}{\varepsilon_k - \lambda_i} |\Phi_i\rangle.$$

Using (7) this can be written as relation (10) where coefficients $C_{\tau p}$ are given by (12). Multiplying (10) from left by $-\varepsilon_k \Delta m_\mu \langle \mu s |$ and using (12) one obtains

$$C_{\mu s} = -\varepsilon_k \Delta m_\mu \sum_{\tau}^{\rho} \sum_p^3 \Omega_{\mu s, \tau p}(\varepsilon_k) C_{\tau p}, \quad \mu = 1, \dots, \rho, \quad s = 1, 2, 3,$$

where $\Omega_{\mu s, \tau p}(\varepsilon)$ is given by (9a). Dividing both sides of this relation by $\varepsilon_k \Delta m_\mu$ one obtains (11). This is a linear set of 3ρ relations in 3ρ unknowns $C_{\tau p}$, and it has a nontrivial solution if and only if determinant of a system (11) vanishes. Thus, one obtains condition (8). This proves that each eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ of relation (6) satisfies (8) and also that the corresponding eigenstate is (10) where coefficients $C_{\tau p}$ satisfy (11). In addition, those coefficients are given by (12). Tracing the above derivation backwards one finds that the inverse is also true. Thus, each root $\varepsilon_k \notin \{\lambda_i\}$ of (8) is an eigenvalue of relation (6). Also, each state (10) where coefficients $C_{\tau p}$ satisfy (11) is the corresponding eigenstate of (6). This proves theorem 1.

One proves theorem 2 along the same lines as theorem 1.

Let λ_j be a η -degenerate unperturbed eigenvalue, and let $|\Phi_{j\kappa}\rangle$ be the corresponding eigenstates. Assume that $\varepsilon_k = \lambda_j$ is an eigenvalue of the perturbed equation (6). We again obtain relation (A.1). However, this time one can divide both sides of this relation with $(\varepsilon_k - \lambda_i)$ where there is a condition $\lambda_i \neq \varepsilon_k$. Multiplying the obtained relation from left by $|\Phi_i\rangle$ and summing over i ($\lambda_i \neq \varepsilon_k$), one has to add to both sides of thus obtained relation quantity $\sum_{\kappa} |\Phi_{j\kappa}\rangle \langle \Phi_{j\kappa} | \mathbf{M} | \Psi_k \rangle$. Now one can use relation (A.2) which gives (15) where coefficients $C_{\tau s}$ and D_{κ} are given by (17). In order to obtain relations (13) and (16) one now multiplies (15) from left by $-\varepsilon_k \Delta m_\mu \langle \mu s |$ and also by $\langle \Phi_{j\kappa} | \mathbf{M}$. Remaining part is similar to the proof of theorem 1.

A.2. Proof of lemma 1

Let the equation (11) have η linearly independent solutions \mathbf{C}^r ($r = 1, 2, 3, \dots, \eta$). Each of these solutions generates according to (10) an eigenstate $|\Psi_k^r\rangle$ of the perturbed eigenvalue equation. All these eigenstates correspond to the same eigenvalue ε_k . Assume that these eigenstates are linearly dependent. Then there exists a nontrivial linear combination of these eigenstates that equals zero:

$$\sum_r^{\eta} c_r |\Psi_k^r\rangle = \sum_i^{3n} \frac{\sum_{\tau}^{\rho} \sum_p^3 \langle \Phi_i | \tau p \rangle \sum_r^{\eta} c_r C_{\tau p}^r}{\varepsilon_k - \lambda_i} |\Phi_i\rangle = 0.$$

Since $|\Phi_i\rangle$ are linearly independent, this implies $\sum_\tau \sum_p \langle \Phi_i | \tau p \rangle \sum_r c_r C_{\tau p}^r = 0$ for each i . Since $|\Phi_i\rangle$ form a complete set, this implies $\sum_\tau \sum_p |\tau p\rangle \sum_r c_r C_{\tau p}^r = 0$. However, vectors $|\tau p\rangle$ are linearly independent, and hence, $\sum_r c_r C_{\tau p}^r = 0$ for each τ and p . This last relation implies that vectors \mathbf{C}^r are linearly dependent, contrary to the assumption. This proves that vectors $|\Psi_k^r\rangle$ must be linearly independent, and hence, degeneracy of each cardinal eigenvalue ε_k equals the number of linearly independent solutions to the matrix equation (11). However, the number of linearly independent solutions to the matrix equation $\mathbf{A}x = 0$ where \mathbf{A} is a square matrix is by definition nullity of this matrix [6]. On the other hand, the rank of a matrix is defined as a number of linearly independent columns, and in the case of a square matrix this equals the number of linearly independent rows [6]. This proves lemma 1, i.e., that the degeneracy of ε_k equals nullity of a matrix $\mathbf{\Omega}(\varepsilon_k) + \Delta\mathbf{M}^{-1}/\varepsilon_k$. In a similar way one proves lemma 2.

A.3. Derivation of relations (19) for nonproper vibrations

Let Φ_{Tx} be a translation in the x -direction. This translation is a linear combination of unit displacements $|\alpha x\rangle$

$$|\Phi_{Tx}\rangle = Q \sum_{\alpha}^n |\alpha x\rangle,$$

where the constant Q is determined by the normalisation condition (3). Using orthonormality relations $\langle \alpha r | \beta t \rangle = \delta_{\alpha\beta} \delta_{rt}$ one finds

$$\begin{aligned} \langle \Phi_{Tx} | \mathbf{M} | \Phi_{Tx} \rangle &= \sum_{\alpha}^n \sum_r^3 m_{\alpha} \langle \Phi_{Tx} | \alpha r \rangle \langle \alpha r | \Phi_{Tx} \rangle \\ &= \sum_{\alpha}^n m_{\alpha} \langle \Phi_{Tx} | \alpha x \rangle \langle \alpha x | \Phi_{Tx} \rangle = Q^2 M = 1 \end{aligned}$$

and similarly for translations in y - and z -direction. Hence, follow the relations (19a).

Let now Φ_{Rz} describe rotation for some small angle ϕ around the z -axis. Displacements in the x - and y -direction of atom α are proportional to $-y_{\alpha}|x_{\alpha}\rangle$ and $x_{\alpha}|y_{\alpha}\rangle$, respectively. The state Φ_{Rz} is, hence, a linear combination

$$|\Phi_{Rz}\rangle = Q \sum_{\alpha}^n [x_{\alpha}|y_{\alpha}\rangle - y_{\alpha}|x_{\alpha}\rangle].$$

Constant Q is again determined by the normalisation condition (3):

$$\begin{aligned} \langle \Phi_{Rz} | \mathbf{M} | \Phi_{Rz} \rangle &= \sum_{\alpha}^n \langle \Phi_{Rz} | x_{\alpha} \rangle m_{\alpha} \langle x_{\alpha} | \Phi_{Rz} \rangle + \sum_{\alpha}^n \langle \Phi_{Rz} | y_{\alpha} \rangle m_{\alpha} \langle y_{\alpha} | \Phi_{Rz} \rangle \\ &= Q^2 \sum_{\alpha}^n (x_{\alpha}^2 + y_{\alpha}^2) m_{\alpha} = Q^2 I_z = 1, \end{aligned}$$

where I_z is moment of inertia around z -axis. Analogous relations are obtained for rotations Φ_{R_x} and Φ_{R_y} . Hence, follow the relations (19b).

A.4. Proof of lemma 3

According to the above derivation of nonproper vibrations, all these vibrations are normalized. It remains to be shown that these vibrations are also orthogonal to each other, provided the coordinate origin is situated in the molecular centre of mass, and provided the coordinate axes coincide with the principal axes of the unperturbed molecule.

One easily shows that translations (19a) are mutually orthogonal. For example,

$$\langle \Phi_{T_x} | \mathbf{M} | \Phi_{T_y} \rangle = \frac{1}{M} \sum_{\alpha\alpha'} \langle \alpha x | m_\alpha | \alpha' y \rangle = 0.$$

Concerning the orthogonality of rotations (19b) to translations (19a) one finds, e.g.,

$$\langle \Phi_{T_x} | \mathbf{M} | \Phi_{R_y} \rangle = -\frac{1}{\sqrt{M I_y}} \sum_{\alpha} m_\alpha z_\alpha$$

and similarly for other possible combinations. If the coordinate origin is situated in the centre of molecular mass, right-hand side of this expression is zero. This shows that the rotations (19b) are orthogonal to the translations (19a), provided the coordinate origin is situated in the molecular centre of mass.

It remains to be shown that rotational states (19b) are orthogonal to each other. Consider, for example, rotations Φ_{R_x} and Φ_{R_y} . One finds

$$\langle \Phi_{R_x} | \mathbf{M} | \Phi_{R_y} \rangle = -\frac{1}{\sqrt{I_x I_y}} \sum_{\alpha} m_\alpha y_\alpha x_\alpha. \quad (\text{A.3})$$

Assume that coordinate axes coincide with the principal axes of a molecule. In this case one coordinate axis has the greatest possible moment of inertia, another has the smallest possible moment of inertia, while the third axis has an intermediate value for the moment of inertia [7]. Let moments of inertia having an extreme value be $I_x = \sum_{\alpha} (y_\alpha^2 + z_\alpha^2) m_\alpha$ and $I_y = \sum_{\alpha} (x_\alpha^2 + z_\alpha^2) m_\alpha$. Since these moments of inertia assume extreme values, they must be stationary with respect to an infinitesimal rotation of coordinate axes, i.e., $\delta I_x = \delta I_y = 0$. Consider an infinitesimal rotation ϕ around z -axis. New coordinates are

$$z' = z, \quad x' = x + \phi y, \quad y' = -\phi x + y,$$

where ϕ is infinitesimal. Hence,

$$\delta I_x = \sum_{\alpha} (y_\alpha'^2 + z_\alpha'^2) m_\alpha - \sum_{\alpha} (y_\alpha^2 + z_\alpha^2) m_\alpha = -2\phi \sum_{\alpha} x_\alpha y_\alpha m_\alpha = 0.$$

In a similar way infinitesimal rotations around x - and y -axis imply

$$\sum_{\alpha} y_{\alpha} z_{\alpha} m_{\alpha} = \sum_{\alpha} z_{\alpha} x_{\alpha} m_{\alpha} = 0.$$

Hence and from (A.3), $\langle \Phi_{Rx} | \mathbf{M} | \Phi_{Ry} \rangle = 0$, and similarly for other rotations. This proves that, provided the coordinate axes coincide with the principal axes, rotations (19b) are mutually orthogonal.

Note that both conditions are necessary in order for improper vibrations (19) to be orthonormalized. It is obvious from the above derivation that if the coordinate system is not in the molecular centre of mass, there is at least one rotation, which is not orthogonal to all translations. Similarly, if the coordinate axes do not coincide with the principal axes, at least one pair of rotations is not mutually orthogonal.

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