On the Definitions of Characteristic Molecular Vibrations and the Distribution of Vibrational Energy

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The relationship of the definition of a completely characteristic normal vibration to the stationary properties of force and compliance constants is examined. The corresponding properties of various distributions of potential, kinetic, and total vibrational energy are described.

As there are different definitions of characteristic vibrations in the literature [1–25] and the term characteristic is often used loosely, we feel it worthwhile to clarify this topic.

The most physically reasonable definition of a completely characteristic normal coordinate seems to be the following: the normal coordinate $\mathbf{Q}_k$ is said to be completely characteristic of the symmetry coordinate $\mathbf{S}_i$ if and only if

$$L_{ik} = (G^{-1})_{ii}^{-1/2}, \quad L_{pk} = 0 \; (\forall p \neq i) \; . \tag{1}$$

Equation (1) is equivalent to the condition

$$(L^{-1})_{ki} = (G^{-1})_{ii}^{1/2}, \quad (L^{-1})_{si} = 0 \; (\forall s \neq k) \; . \tag{2}$$

A strictly analogous definition of a completely characteristic normal force can also be given. The normal force $\mathbf{f}_k{}^N$ is said to be completely characteristic of the generalized symmetry force $\mathbf{f}_i$ if and only if

$$L_{ik} = G_{ii}^{1/2}, \quad L_{is} = 0 \; (\forall s \neq k) \; . \tag{3}$$

Equation (3) is equivalent to the condition

$$(L^{-1})_{ki} = G_{ii}^{-1/2}, \quad (L^{-1})_{kp} = 0 \; (\forall p \neq i) \; . \tag{4}$$

Usually, an accepted form of definition of the potential energy distribution (P. E. D.), kinetic energy distribution (K. E. D.), and recently of the total energy distribution [24–25] (T. E. D.) is used to interpret the degree of mixing of the symmetry coordinates $\mathbf{S}_i$ in any normal mode of vibration.

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The choice of the parameters (such as force constants, compliance constants, symmetry coordinates, etc) among which the potential energy $V^{(k)}$, the kinetic energy $T^{(k)}$ and the total energy $E^{(k)}$ of a normal vibration $\mathbf{Q}_k$ can be distributed is somewhat arbitrary. Several different distributions are examined below in the light of our definition of a completely characteristic vibration. Finally, we relate that definition to the concept of a characteristic set of symmetry coordinates advocated by Herranz et alias [10, 22].

a) – P. E. D. among $n(n+1)/2$ distinct force constants F_{ij} $(j = 1, \ldots, n; \; i \leqq j)$.

The P. E. contribution $V^{(k)}(F)_{ij}$ associated with F_{ij} in the k-th frequency is

$$V^{(k)}(F)_{ij} \equiv (2 - \delta_{ij}) \, L_{ik} \, L_{jk} \, F_{ij} \, \Lambda_k{}^{-1} \, . \tag{5}$$

$V^{(k)}(F)_{ij}$ is invariant to scaling changes and, since

$$\sum_{i} \sum_{\substack{j \\ (i \leq j)}} V^{(k)}(F)_{ij} = 1 \; (\forall k) \, , \tag{6}$$

$V^{(k)}(F)_{ij}$ represents the fraction of the P. E. of the k-th frequency associated with F_{ij} .

The disadvantage of a definition [6] that omits the factor $\Lambda_k{}^{-1}$ from Eq. (5) is that the sum of such unnormalized contributions is Λ_k, not unity. Omission of the factor $(2 - \delta_{ij})$ from Eq. (5) corresponds to defining a P. E. D. among n^2 force constants and to regarding F_{ij} and F_{ji} as distinct: this variant has no special advantage over Eq. (5) above.

The analogue of Eq. (5) for the K. E. D. among $\mathbf{G}^{-1}$ elements is

$$T^{(k)}(G^{-1})_{ij} \equiv (2-\delta_{ij}) L_{ik} L_{jk} (G^{-1})_{ij}; \quad j=1,\ldots,n; \quad i \leqq j. \quad (7)$$

The contributions $T^{(k)}(G^{-1})_{ij}$ are invariant to scaling changes [7] and their sum is unity:

$$\sum_{i} \sum_{\substack{j \\ (i \leq j)}} T^{(k)}(G^{-1})_{ij} = 1 \ (\forall k) . \quad (8)$$

Finally, the T. E. D. among the $\mathbf{F}$ and $\mathbf{G}^{-1}$ elements is given by [24]

$$E^{(k)}(F, G^{-1})_{ij} = [V^{(k)}(F)_{ij} + T^{(k)}(G^{-1})_{ij}]/2 \quad (9)$$

that is

$$E^{(k)}(F, G^{-1})_{ij} = \frac{(2-\delta_{ik})}{2} [F_{ij} \Lambda_k^{-1} + (G^{-1})_{ij}] L_{ik} L_{jk} . \quad (10)$$

Therefore, for a completely characteristic normal coordinate $\mathbf{Q}_k$ it follows from Eqs. (1), (5), (7) and (10) that [14, 18, 24]

$$V^{(k)}(F)_{ii} = 1 , \quad (11\,a)$$

$$V^{(k)}(F)_{ij} = 0 \ (\forall i \neq j) , \quad (11\,b)$$

$$T^{(k)}(G^{-1})_{ii} = 1 , \quad (12\,a)$$

$$T^{(k)}(G^{-1})_{ij} = 0 \ (\forall i \neq j) , \quad (12\,b)$$

and

$$E^{(k)}(F, G^{-1})_{ii} = 1 , \quad (13\,a)$$

$$E^{(k)}(F, G^{-1})_{ij} = 0 \ (\forall i \neq j) . \quad (13\,b)$$

It should be noted that Eq. (11 a) or (12 a) or (13 a) alone does not necessarily specify a completely characteristic normal coordinate $\mathbf{Q}_k$. The "Potential energy criterion" of Becher and Ballein [26] exemplifies this fact.

Taylor has shown [7] that, if contributions $V^{(k)}(F)_{ii}$ and $T^{(k)}(G^{-1})_{ii}$ predominate in Eqs. (11) and (12), then both such contributions approach unity and, in the limit,

$$\Lambda_k \rightarrow F_{ii}(G^{-1})_{ii}^{-1} \quad (14)$$

represents the frequency that characterizes this fully decoupled k-th vibration which then involves only the symmetry coordinate $\mathbf{S}_i$. It was later shown [14] that the formula

$$F_{ii} = \Lambda_k (G^{-1})_{ii} \quad (k=1,\ldots,n) \quad (15)$$

describes the n stationary values of F_{ii}, each of which pertains to a normal frequency $\Lambda_k (k=1, \ldots, n)$ that corresponds to a fully decoupled symmetry coordinate $\mathbf{S}_i$. The necessary and sufficient condition for F_{ii} to possess the stationary values of Eq. (15) is given by Eq. (1) or (2).

b) – P. E. D. among $n(n+1)/2$ distinct compliance constants C_{ij}. The P. E. contribution $V^{(k)}(C)_{ij}$ associated with C_{ij} in the k-th frequency is [14, 20]

$$V^{(k)}(C)_{ij} \equiv (2-\delta_{ij}) (L^{-1})_{ki} (L^{-1})_{kj} C_{ij} \Lambda_k \quad (16)$$

in which $C_{ij} \equiv (F^{-1})_{ij}$. $V^{(k)}(C)_{ij}$ is invariant to scaling changes and, since

$$\sum_{i} \sum_{\substack{j \\ (i \leq j)}} V^{(k)}(C)_{ij} = 1 \ (\forall k) , \quad (17)$$

it follows that $V^{(k)}(C)_{ij}$ represents the fraction of the potential energy of the k-th frequency associated with C_{ij}.

The equation [14]

$$C_{ii} = G_{ii} \Lambda_k^{-1} \quad (k=1,\ldots,n) \quad (18)$$

describes the n stationary values of C_{ii}, each of which pertains to a normal frequency $\Lambda_k (k=1, \ldots, n)$ that corresponds to a fully decoupled symmetry force $\mathbf{f}_i$. The necessary and sufficient condition for C_{ii} to possess the stationary values of Eq. (18) is given by Eq. (3) or (4).

The K. E. D. among $\mathbf{G}$ elements $[T^{(k)}(G)_{ij}]$, and the T. E. D. among $\mathbf{C}$ and $\mathbf{G}$ elements $[E^{(k)}(C,G)_{ij}]$ can easily be defined [24]. Then, for a completely characteristic normal force $\mathbf{f}_k^N$ would follow conditions analogous to Equations (11), (12), and (13).

c) – P. E. D., K. E. D. and T. E. D. among n symmetry coordinates $\mathbf{S}_i$ $(i=1,\ldots,n)$.

The potential, kinetic, and total energy contributions, $V_i^{(k)}$, $T_i^{(k)}$ and $E_i^{(k)}$, respectively, associated with $\mathbf{S}_i$ in the k-th frequency are defined as [9, 11, 17, 20, 23, 24]

$$V_i^{(k)} \equiv \sum_{j=1}^{n} L_{ik} L_{jk} F_{ij} \Lambda_k^{-1} = L_{ik} (L^{-1})_{ki} , \quad (19)$$

$$T_i^{(k)} \equiv \sum_{j=1}^{n} L_{ik} L_{jk} (G^{-1})_{ij} = L_{ik} (L^{-1})_{ki} , \quad (20)$$

and

$$E_i^{(k)} \equiv [V_i^{(k)} + T_i^{(k)}]/2 = L_{ik} (L^{-1})_{ki} . \quad (21)$$

These equal quantities, denoted $M_i^{(k)}$, obey the relationships

$$\sum_{i} M_i^{(k)} = 1 , \ \sum_{k} M_i^{(k)} = 1 , \ \sum_{i} \sum_{k} M_i^{(k)} = n \quad (22)$$

and are invariant to scaling changes. $M_i^{(k)}$ can be regarded as the fractional contribution from each $\mathbf{S}_i$ to the energy of the k-th frequency.

Only in the 2×2 case is the matrix $\mathbf{M}$ with elements given by $M_{ij} \equiv M_i^{(j)}$ necessarily symmetric[17-19]. In the general case the choice of $\mathbf{L} = \mathbf{G}^{1/2}$ ensures that $M_i^{(k)} = M_k^{(i)}$, but the converse is not true.

If the normal coordinate $\mathbf{Q}_k$ is completely characteristic of the symmetry coordinate $\mathbf{S}_i$, it follows from Eqs. (1), (2), and (19) – (21) that[19, 23, 24]

$$M_i^{(k)} = 1\,, \quad M_j^{(k)} = 0\ (\forall j \neq i)\,. \tag{23}$$

But the converse is not always true; i. e. Eq. (23) is not generally a sufficient condition for $\mathbf{Q}_k$ to be completely characteristic of $\mathbf{S}_i$. For example, if $\mathbf{L}$ is lower triangular (see References[12-14, 17-20, 23-24]) it follows that

$$M_i^{(k)} = \delta_{ik}\ (\forall i, \forall k)\,. \tag{24}$$

However, in this example, only one normal coordinate is completely characteristic of a particular symmetry coordinate; specifically, $\mathbf{Q}_n$ is then completely characteristic of $\mathbf{S}_n$ because $L_{jn} = 0\,(\ j \neq n)$; [see Eq. (1)]. The failure of Eq. (24) to guarantee that $\mathbf{Q}_k$ is completely characteristic of $\mathbf{S}_i$ is a disadvantage of defining the P. E., K. E. and T. E. as distributed among the n symmetry coordinates according to Equations (19) – (21).

d) – Characteristic set of symmetry coordinates. Of all sets of symmetry coordinates $\mathbf{S}' = \mathbf{U} \cdot \mathbf{S}$ related to a given set $\mathbf{S}$ by orthogonal transformations $\mathbf{U}$, the set

$$\mathbf{S}_c = \mathbf{U}_c \cdot \mathbf{S} \tag{25}$$

for which the corresponding normal coordinate transformation $\mathbf{L}_c = \mathbf{U}_c \cdot \mathbf{L}$ is symmetric and has its trace maximized is designated by Herranz et al.[10, 22] as the "characteristic set of symmetry coordinates." The connection between this characteristic set defined by Herranz et al. and the single symmetry coordinate defined in our Eq. (1) or (2) for a completely characteristic vibration is remote, except perhaps for the following analogy: if $\mathbf{Q}_t$ is completely characteristic of $\mathbf{S}_t$ in the sense of Eq. (2) then $(L^{-1})_{tt}$ is maximal, whereas if $\mathbf{S}_c$ is the characteristic set in the sense of Eq. (25) then $\sum_t (L^{-1})_{tt}$ is maximal. Even this analogy is slightly misleading in that the maximal property of $(L^{-1})_{tt}$, but not that of $\sum_t (L^{-1})_{tt}$, is independent of scaling. The suggestion of Herranz et al.[22] that the elements (or their squares) of $\mathbf{V}_c = \tilde{\mathbf{L}} \cdot \mathbf{G}^{-1/2}$ be used instead of the P. E. D. among n symmetry coordinates would entail sacrificing to desirable invariance to scaling of the P. E. D. quantities.

In conclusion we emphasize that schemes for partitioning the vibrational energy of a normal frequency among coupled symmetry coordinates (or their force constants, etc...) are somewhat artificial and are, at best, only roughly descriptive visualizations of the normal coordinate transformation itself. The case of a normal coordinate that is completely characteristic of one symmetry coordinate is exceptional and represents the accidental splitting off from the secular equation of a fully decoupled one dimensional factor.

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