Vibrational Total Energy Distributions in Terms of Symmetry Coordinates, Forces and Momenta

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Z. Naturforsch. **35a**, 464–465 (1980);
received November 12, 1979

The fundamental definitions of the Total Energy and of the Vibrational Total Energy Distributions are presented in details in terms of either symmetry coordinates, or generalised symmetry forces, or generalized symmetry coordinates. This, give now a uniform tool for physicists and chemists in the field of characterisation of the normal vibrational modes of polyatomic molecules.

The definitions of the Total Energy Distributions, hereafter abbreviated as TED, have been the subject of many works in recent years [1–9]. Several of the published papers present different aspects of the same fundamental concepts formulated in different words and notations, and in some cases it may seem that there are contradictory discussions and interpretations. We feel that it is necessary now to clarify the situation in order to give a uniform tool for physicists and chemists in the field of characterisation of the normal vibrational modes of polyatomic molecules.

This communication principally deals with fundamental definitions. In particular, the derivation of the TED with symmetry forces as an alternative basis to symmetry coordinates is given, and the possibility of using momenta is introduced. Further comments on the TED-method will be found elsewhere [9].

TED in Terms of Contributions from Symmetry Coordinates

Summation of the standard formulae [10] for the potential and kinetic energies in terms of symmetry coordinates, S_i, and velocities $\dot{S}_i$, yields the total energy for the kth normal mode of vibration in the form

$$2E^{(k)} = \tilde{\boldsymbol{S}}^{(k)} \boldsymbol{F} \boldsymbol{S}^{(k)} + \tilde{\dot{\boldsymbol{S}}}^{(k)} \boldsymbol{G}^{-1} \dot{\boldsymbol{S}}^{(k)} . \tag{1}$$

When the values of the coordinates, $S_i{}^{(k)} = L_{ik} Q_k$ and $Q_k = \mathring{Q}_k \cos(\lambda_k{}^{1/2} t + \varepsilon_k)$, and the corresponding velocities are introduced, one obtains

$$2E^{(k)} = \lambda_k \mathring{Q}_k{}^2 \Big[\cos^2(\lambda_k^{1/2} t + \varepsilon_k) \sum_i \sum_j F_{ij} \lambda_k^{-1} L_{ik} L_{jk} + \sin^2(\lambda_k^{1/2} t + \varepsilon_k) \sum_i \sum_j (\boldsymbol{G}^{-1})_{ij} L_{ik} L_{jk}\Big] . \tag{2}$$

Now, $E_{ij}^{(k)}(\boldsymbol{S}, \dot{\boldsymbol{S}})$ is defined as the mean value, i.e., average over one period, of the contribution to the total energy from the displacements S_i and S_j and the velocities $\dot{S}_i$ and $\dot{S}_j$. This procedure leads to TED in the form

$$2E^{(k)} = \Big[\sum_i \sum_j E_{ij}^{(k)}(\boldsymbol{S}, \dot{\boldsymbol{S}})\Big] \lambda_k \mathring{Q}_k{}^2 , \tag{3}$$

with

$$E_{ij}^{(k)}(\boldsymbol{S}, \dot{\boldsymbol{S}}) = (F_{ij} \lambda_k^{-1} + (\boldsymbol{G}^{-1})_{ij}) L_{ik} L_{jk}/2 = [V_{ij}^{(k)}(\boldsymbol{S}) + T_{ij}^{(k)}(\dot{\boldsymbol{S}})]/2 . \tag{4}$$

The connection with the equivalent results given previously [1–7] is

$$E_i^{(k)}(\boldsymbol{S}, \dot{\boldsymbol{S}}) = E_i^{(k)} = E^{(k)}_{(\boldsymbol{F}, \boldsymbol{G}^{-1})_i} \quad \text{(principal contributions of } S_i \text{ and } \dot{S}_i\text{)}, \tag{5}$$

$$E_{ij}^{(k)}(\boldsymbol{S}, S) = E_{ij}^{(k)} = E^{(k)}_{(\boldsymbol{F}, \boldsymbol{G}^{-1})_{ij}} \quad \text{(coupling contributions of } S_i, S_j, \dot{S}_i \text{ and } \dot{S}_j\text{)}$$

TED in Terms of Generalised Symmetry Forces

Application of the definitions of the generalised symmetry and normal forces, $\boldsymbol{f} = -\boldsymbol{FS}$ and $\boldsymbol{f}^Q = -\boldsymbol{\Lambda Q}$, linked together by the relation $\boldsymbol{f} = \tilde{\boldsymbol{L}}^{-1} \boldsymbol{f}^Q$ [11, 12], gives

$$2E = \tilde{\boldsymbol{f}} \boldsymbol{C} \boldsymbol{f} + \tilde{\dot{\boldsymbol{f}}} (\boldsymbol{C} \boldsymbol{G}^{-1} \boldsymbol{C}) \dot{\boldsymbol{f}} . \tag{6}$$

Similar to the treatment for symmetry coordinates, $E_{ij}^{(k)}(\boldsymbol{f}, \dot{\boldsymbol{f}})$ is taken as the mean value of the total energy in terms of the generalised symmetry forces and their time derivatives:

$$2E^{(k)} = \Big[\sum_i \sum_j E_{ij}^{(k)}(\boldsymbol{f}, \dot{\boldsymbol{f}})\Big] \lambda_k^{-1} \mathring{f}_k^{Q^2} \tag{7}$$

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and

$$E_{ij}^{(k)}(\boldsymbol{f},\dot{\boldsymbol{f}}) = (C_{ij}\,\lambda_k + (\boldsymbol{C}\,\boldsymbol{G}^{-1}\,\boldsymbol{C})_{ij}\,\lambda_k{}^2) \cdot (\boldsymbol{L}^{-1})_{ki}\,(\boldsymbol{L}^{-1})_{kj}/2 = [V_{ij}^{(k)}(\boldsymbol{f}) + T_{ij}^{(k)}(\dot{\boldsymbol{f}})]/2\,. \tag{8}$$

Errors in previous work [2, 3] should be corrected in accordance with Eqs. (6) and (8).

TED in Terms of Generalised Symmetry Momenta

The kinetic energy part of Eq. (6) may be substituted by a quadratic form in momenta [10, 12]. Then the total energy becomes

$$2\,E = 2\,V + 2\,T = \tilde{\boldsymbol{f}}\boldsymbol{C}\boldsymbol{f} + \tilde{\boldsymbol{P}}\boldsymbol{G}\,\boldsymbol{P} = \tilde{\dot{\boldsymbol{P}}}\,\boldsymbol{C}\,\dot{\boldsymbol{P}} + \tilde{\boldsymbol{P}}\boldsymbol{G}\,\boldsymbol{P}\,, \tag{9}$$

with the last part being a consequence of Newtons second law: $\boldsymbol{f} = \dot{\boldsymbol{P}}$. Substitution of $\boldsymbol{P} = \tilde{\boldsymbol{L}}^{-1}\boldsymbol{P}^Q$ and $\dot{\boldsymbol{P}} = \tilde{\boldsymbol{L}}^{-1}\dot{\boldsymbol{P}}^Q$ and taking the time average as in the two sections above, result in the TED expressed as

$$E_{ij}^{(k)}(\dot{\boldsymbol{P}},\boldsymbol{P}) = (C_{ij}\,\lambda_k + G_{ij})\,(\boldsymbol{L}^{-1})_{ki}\,(\boldsymbol{L}^{-1})_{kj}/2 = [V_{ij}^{(k)}(\dot{\boldsymbol{P}}) + T_{ij}^{(k)}(\boldsymbol{P})]/2\,. \tag{10}$$

This total energy distribution element can also be denoted $E_{ij}^{(k)}(\boldsymbol{f},\,\boldsymbol{P})$ or $E^{(k)}_{(\boldsymbol{C},\,\boldsymbol{G})_{ij}}$. The last symbol erroneously was used to signify the energy contributions from generalised forces [2, 3]. It is seen from Eq. (10) that it is more correct to speak about contribution from the momenta, or from forces (in the V part) and momenta (in the T part).

Finally, it easily can be shown that summation under the index j, for all the three TED expressions (4), (8) and (10) gives the unique result

$$\sum_j E_{ij}^{(k)}(\boldsymbol{S},\dot{\boldsymbol{S}}) = \sum_j E_{ij}^{(k)}(\boldsymbol{f},\dot{\boldsymbol{f}}) = \sum_j E_{ij}^{(k)}(\dot{\boldsymbol{P}},\boldsymbol{P}) = L_{ik}\,(\boldsymbol{L}^{-1})_{ki} \equiv M_i{}^{(k)}. \tag{11}$$

This distribution has been called the PKTED since the result is valid separately for the potential and kinetic energy parts of the TED. It is warned, however, against the use of Eq. (11) in the classification of normal modes, since the equation implies a redistribution of the coupling terms which frequently lead to conclusions in conflict with experience [5]. It can be concluded that choice of basis for the Total Energy Distribution is crucial and, therefore, always must be selected with care.

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