ON EXACT AND APPROXIMATE NATURAL COORDINATES IN THE THEORY OF VIBRATIONS OF POLYATOMIC MOLECULES

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Abstract

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ON EXACT AND APPROXIMATE NATURAL COORDINATES IN THE THEORY OF VIBRATIONS OF POLYATOMIC MOLECULES

At the present time, in the study of the vibrational spectra of molecules, it is becoming essential to take into account a number of subtle effects, which makes it necessary to refine the theory of vibrations of polyatomic molecules. One of the questions requiring consideration is that of the system of vibrational coordinates.

Any instantaneous configuration of a molecule can be described by a set of instantaneous values $s, \alpha, \ldots$ of bond lengths, valence angles, etc.; therefore it is natural to choose as vibrational coordinates the changes $Q = s - s_0$, $\gamma = \alpha - \alpha_0, \ldots$ of the corresponding geometrical parameters ([1,2]); for the equilibrium configuration these changes vanish. The potential energy of vibrations is then represented in the form of a series in powers of the coordinates introduced, which we shall call **exact natural vibrational coordinates**; in the harmonic approximation only the quadratic terms of the series are taken into account, whose coefficients form the matrix of force constants U. However, in the theory of molecular vibrations the natural vibrational coordinates are usually introduced somewhat differently, namely as linear functions of the differences of the displacements $\mathbf{r}_i$ of atoms from their equilibrium positions. The connection between such coordinates and the displacements of the atoms is expressed by the relation

$$q^{(0)} = \mathbf{B}(0)\mathbf{r}, \tag{1}$$

where $\mathbf{B}(0)$ is a time-independent vector matrix containing the equilibrium unit vectors of the molecule and effecting the linear transformation from the atomic displacements $\mathbf{r}_i$ to the vibrational coordinates $q_j^{(0)}(Q^{(0)}, \gamma^{(0)}, \ldots)$. We shall call these coordinates **approximate natural vibrational coordinates**, since they coincide with the changes $q(Q = s - s_0, \gamma = \alpha - \alpha_0, \ldots)$ of the equilibrium geometrical parameters of the molecule only in the limiting case of infinitely small displacements.

The distinction between exact and approximate natural coordinates cannot be neglected when solving the vibrational problem with allowance for anharmonicity. This distinction is manifested also in the fact that, when approximate natural coordinates are used, isotopic substitution leads to a small dependence of the force constants on the atomic masses, as was first noted in ([3]), where, however, this effect did not receive a satisfactory explanation. The correct explanation is that approximate natural coordinates, in contrast to exact ones, are not, strictly speaking, purely internal, completely independent of the motion of the molecule as a whole. But they possess the important advantage that they make it possible to represent exactly the kinetic energy in the form of a quadratic form with constant coefficients, which are expressed explicitly through scalar products of unit vectors characterizing the equilibrium configuration of the molecule.

Indeed, the kinetic energy in an arbitrary system of vibrational coordinates has the form

$$T_{\text{kin}} = {}^1/_2\, \tilde{p}\mathbf{B}\varepsilon\mathbf{B}p = {}^1/_2\tilde{p}Tp, \tag{2}$$

where $\tilde{p}$ and p are the row matrix and column matrix of the momenta p_j conjugate to the chosen coordinates q_j; $\mathbf{B}$ is a vector matrix expressing the generalized velocities $\dot{q}_j$ in terms of the derivatives $\dot{\mathbf{r}}_i$ of the instantaneous displacements of the atoms from their equilibrium positions; ε is the diagonal matrix of the reciprocal atomic masses. In the case of approximate natural coordinates, it follows from (1), in view of the time independence of $\mathbf{B}(0)$, that

$$\dot{q}^{(0)} = \mathbf{B}(0)\dot{\mathbf{r}}. \tag{3}$$

In (2) one must put $\mathbf{B} = \mathbf{B}(0)$, $p = p^{(0)}$, $T = T(0)$, and the coefficients of the quadratic form $T_{\text{kin}} = \frac{1}{2}\tilde{p}^{(0)}T(0)p^{(0)}$ are immediately obtained explicitly as the elements of the matrix $T(0) =$

$$= \mathbf{B}(0)\varepsilon\widetilde{\mathbf{B}}(0).$$

The situation is more complicated when exact natural coordinates are introduced. In this case the matrix $\mathbf{B}$ in expression (2) is a function of time, and

$$\dot{q} = \mathbf{B}(t)\dot{\mathbf{r}}, \tag{4}$$

where, in contrast to (3), where $\mathbf{B}(0)$ refers to the equilibrium configuration, $\mathbf{B}(t)$ contains unit vectors characterizing the instantaneous configuration and changing their orientation in the moving coordinate system attached to the molecule.

Fig. 1

Fig. 1

Figure 1: Fig. 1

For example, for the stretching of a bond (see Fig. 1),

$$s(t)\mathbf{e}(t) = (s_0 + Q)\mathbf{e}(t) = s_0\mathbf{e}(0) + (\mathbf{r}_2 - \mathbf{r}_1), \tag{5}$$

and differentiation with respect to time gives

$$\dot{s}(t)\mathbf{e}(t) + s(t)\dot{\mathbf{e}}(t) = \dot{Q}\mathbf{e}(t) + (s_0 + Q)\dot{\mathbf{e}}(t) = \dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1. \tag{6}$$

Since $\mathbf{e} \perp \dot{\mathbf{e}}$, we obtain

$$\dot{Q} = \mathbf{e}(t)(\dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1). \tag{7}$$

In accordance with (2), the elements of the matrix $T(t) = \mathbf{B}(t)\varepsilon\widetilde{\mathbf{B}}(t)$ will be linear combinations of scalar products of unit vectors; these linear combinations are invariant with respect to translational motion and rotation of the molecule as a whole, but depend on time. The matrix $T(t)$ may be represented in the form

$$T(t) = T(0) + \Delta T(t), \tag{8}$$

where $T(0) = \mathbf{B}(0)\varepsilon\widetilde{\mathbf{B}}(0)$ is the constant matrix obtained at the equilibrium values of the geometrical parameters of the molecule, while $\Delta T(t)$ is a time-dependent correction. For small vibrations the corresponding correction

$$\Delta T_{\text{kin}} = \frac{1}{2}\tilde{p}\Delta T(t)p \tag{9}$$

to the kinetic energy

$$T_{\text{kin}}^{(0)} = \frac{1}{2}\tilde{p}T(0)p = \frac{1}{2}p\mathbf{B}(0)\varepsilon\widetilde{\mathbf{B}}(0)p \tag{10}$$

may be neglected, all the more since $\Delta T(t)$ reaches its maximum at the amplitude values of the vibrations, when the quantities p decrease to zero. However, if the vibrations cannot be considered small and it is necessary to take their anharmonicity into account, this correction must be included in solving the vibrational problem in exact natural coordinates. We note that for sufficiently small vibrations, when one may put $\mathbf{B}(t) \approx \mathbf{B}(0)$, relation (4) reduces to relation (3), and integration of the latter gives the dependence (1), i.e., we arrive at approximate natural coordinates.

Let us now consider the question of the form of the matrix of force constants depending on whether exact or approximate natural coordinates are used. In a system of exact natural coordinates the potential energy in the quadratic approximation can be written in the form

$$U_{\text{pot}} \approx {}^1/_2 \tilde{q} U q, \tag{11}$$

where U is the matrix of force constants, and the derivatives

$$-\partial U_{\text{pot}} / \partial q_j = f_j = dp_j/dt \tag{12}$$

give the generalized forces corresponding to the coordinates q_j. The forces $\mathbf{f}_i$ acting, during vibrations, on the atoms of the molecule are found by differentiating with respect to time the relation for the momenta

$$\mathbf{p} = \tilde{\mathbf{B}}(t)p, \tag{13}$$

corresponding to relation (4) for the velocities in the system of exact natural coordinates. We obtain

$$\mathbf{f} = \dot{\tilde{\mathbf{B}}}(t)p + \tilde{\mathbf{B}}(t)f = \mathbf{f}_{\text{cor}} + \mathbf{f}_{\text{pot}}. \tag{14}$$

Here $\mathbf{f}$ is the column matrix of the forces $\mathbf{f}_i$, and f is the column matrix of the generalized forces f_j. The first term $\mathbf{f}_{\text{cor}} = \dot{\tilde{\mathbf{B}}}(t)p$ gives the nonpotential Coriolis forces arising in the molecule during vibrations as a result of rotations of the bonds relative to one another. The second term $\mathbf{f}_{\text{pot}} = \tilde{\mathbf{B}}(t)f$ describes the potential forces acting on the atoms of the molecule when the equilibrium configuration is changed, and in the quadratic approximation (11)

$$\mathbf{f}_{\text{pot}} = -\tilde{\mathbf{B}}(t)Uq. \tag{15}$$

To clarify the physical aspect of the question, let us examine the case in which the matrix U is diagonal. When only one of the bonds is stretched, a pair of forces arises, equal in magnitude and opposite in sign, acting on the atoms of the bond under consideration along its instantaneous direction $\mathbf{e}(t)$. This direction in the general case will not coincide with the direction of the equilibrium unit vector of the bond $\mathbf{e}(0)$, unless the center of gravity of the molecule lies on the straight line passing through the bond. This circumstance is well known, and it must be taken into account when calculating intensities in vibrational spectra (4).

In the system of approximate natural coordinates

$$\mathbf{p} = \tilde{\mathbf{B}}(0)p^{(0)}, \tag{16}$$

and for the forces acting on the atoms during vibrations we obtain

$$\mathbf{f} = \mathbf{f}^{(0)}_{\text{pot}} = -\tilde{\mathbf{B}}(0)U^{(0)}q^{(0)}, \tag{17}$$

where $U^{(0)}$ is the matrix of force constants in approximate natural coordinates. If the matrix $U^{(0)}$ is also formally chosen to be diagonal and numerically equal to the matrix U (which corresponds to a modified force field), then, under an analogous deformation of stretching of one of the bonds, forces will act on the atoms of this bond along the equilibrium unit vector $\mathbf{e}(0)$, differing in direction from the real forces (15) by an angle which, for small vibrations, is a small quantity of the same order as the coordinates themselves. This angle will be maximal at amplitude values of the vibrational coordinates, when the difference between the directions of the unit vectors for the exact and approximate coordinate systems is greatest.

When solving the vibrational problem in approximate natural coordinates, which, as already noted, are not purely internal coordinates, the matrix $U^{(0)}$ will define a certain effective force field specified in the system of equilibrium unit vectors connected with the molecule and differing from the force field obtained when solving the pro-

problem in exact vibrational coordinates. For example, in the example considered, when the matrix U is diagonal and only one bond is stretched in the direction $\mathbf{e}(t)$, the components of the force perpendicular to the equilibrium direction of the bond $\mathbf{e}(0)$ must differ from zero, which is possible only if $U^{(0)}$ has off-diagonal elements. Thus, a diagonal matrix U will already correspond to a nondiagonal matrix $U^{(0)}$.

The relation between U and $U^{(0)}$ cannot be established independently of the instantaneous configuration of the molecule during vibrations, since the connection between exact and approximate natural coordinates depends on time, and this connection is nonlinear. However, for small vibrations the difference between the matrices U and $U^{(0)}$ will be small, and it may either be completely neglected or taken into account approximately, on the basis of the requirement that the system of forces acting on the atoms under deformations of the molecule coincide in the case of exact and in the case of approximate natural vibrational coordinates at their amplitude values.

Because the matrix $U^{(0)}$ corresponds to a system of approximate, rather than exact, natural coordinates, its elements prove to depend on the masses of the atoms; in particular, they will change under isotopic substitution ([3,6]), although only slightly (by 2–3% when H is replaced by D).

Taking account of the distinction between the exact and approximate systems of natural vibrational coordinates will be especially important in considering the anharmonicity of vibrations of polyatomic molecules, and a more detailed investigation of this question is necessary as applied to the case of vibrations that can no longer be regarded as small.

In addition, the distinction between exact and approximate natural coordinates is of fundamental importance when dependent coordinates are used. In this case only linear relations can exist between the approximate coordinates, whereas the relations between the exact coordinates will in general be nonlinear. This circumstance must be taken into account, in particular, in solving a problem with a potential field of the Urey-Bradley type.

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Note: Figure translations are in progress. See original paper for figures.