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An approach to a realistic visualization of curvilinear molecular vibrations

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Abstract

We develop the theoretical tools for a realistic visualization of curvilinear molecular vibrations. We transform the internal coordinates of a molecule into Cartesian coordinates. The transformation of curvilinear coordinates quickly gives complicate differential geometrical expressions.

We describe the mathematical formalism on a low level of the corresponding power expansions. We present a computer program which uses the derived formulas and computes data for an animation of the trajectories of the vibrations.

1. Introduction

Modern molecular theoretical methods include potential energy minimization and techniques of vibrational normal modes analysis. They open the possibility to understand the complex pattern of molecular systems. These procedures also allow treatments of systems which are not, or only partly, tractable by experimental chemical methods. An interesting aspect of molecular theoretical research is the treatment of molecular processes above the normal modes. For example, we can get insights in the behaviour of bonds or into reaction dynamics, if we know the behaviour of vibrations.

The theoretical understanding of vibrations is based on calculations of the corresponding force

constants the exactness of which should be very high. In this field, there are great improvements in the last years. There are empirical calculations of force fields of a quality being acceptable. The problem is that force constants are derived via perturbation theory from complex experimental data [1]. On the other hand, force constants can also be calculated with quantum mechanical (non empirical) methods. But, the tributes to this way are enormous costs for computer time especially if we include the electron correlation. Today, quantum chemical program systems are very powerful tools for quite exact calculations of force fields [2,3].

A parallel development to these direct methods points in the direction of a suitable interpretation or summarized explanation of the huge amount of calculated data. The many possibilities of computer graphics for visualization are one way. Program systems for quantum chemistry [4] include

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modules for interpretation of the results which reach for normal modes a good level of imaginary power. However, the straight normal modes tend to exaggerate highly the animated picture [5].

This paper deals with the next step: The inclusion of the vibrational behaviour via a realistic animation of real curvilinear vibrations. The visualization of vibrations of a molecule on the screen of a PC, or of a work station for greater molecules, can be a piece of the bridge to understand the mechanisms of chemical reactions. Unimolecular reactions can result directly from highly excited vibrations [6,7]. The importance of programs for molecular modelling can be raised, if we couple their results with vibrational events [8].

The spatial extension of a molecule is modified by its vibrations, and this holds already near the absolute zero of the temperature scale. An important question is: do certain molecules agree with some reactive holes, reactive centers of other greater molecules, like a key in a lock? The answer depends on the spatial extension of the key and lock molecules. Such kinds of problems are treated in pharmacological research for drug design using molecular modelling programs [8,9]. Also, in the field of zeolite research, we find widespread use of molecular modelling. Those investigations are the aim which allow to decide which zeolite adsorb and can be a molecular sieve in the course of a separation process. The question is, if or if not certain small molecules can selectively pass the cages of the zeolite [10].

The start that this paper gives towards the solution is the following. For a realistic visualization of vibrations we have to transform the natural, curvilinear coordinates of a molecule, the internal ones, into Cartesian coordinates. The step is not to avoid, because the points of a picture on the screen are calculated via the Cartesian coordinates of the screen. But, the internal coordinates are curvilinear; and the transformation of curvilinear coordinates quickly gives quite complicate differential geometrical expressions [11]. In this paper we describe the mathematical formalism on a low level of the corresponding power series expansions. And next, we describe a computer program which uses the arrived formulas and

computes data files for an animation of the interesting vibrations.

2. Theory

To make an animation of molecular vibrations, we have to solve the Lagrange equations of motion, and also we have to solve the Schrödinger equation. But, the first step in the formulation of these equations is the development of kinetic and potential energy, and of the Hamiltonian using internal coordinates \mathbf{q} . The kinetic energy is given by the quadratic form

$$T = \frac{1}{2} \frac{dq^k}{dt} g_{kn} \frac{dq^n}{dt} \quad (1)$$

The elements g_{kn} mean the rank-2 covariant metric tensor. We use the Einstein summation convention: it is to sum over any repeated upper and lower indices. The potential energy is given, in the general case, by a series expansion in powers of the internal coordinates.

$$V = V(\mathbf{q}_e) + \frac{\partial V(\mathbf{q}_e)}{\partial q^k} \Delta q^k + \frac{1}{2} \frac{\partial^2 V(\mathbf{q}_e)}{\partial q^k \partial q^n} \Delta q^k \Delta q^n + \frac{1}{6} \frac{\partial^3 V(\mathbf{q}_e)}{\partial q^k \partial q^n \partial q^r} \Delta q^k \Delta q^n \Delta q^r + \dots \quad (2)$$

The first term of the r.h.s., the absolute term, can be omitted. It has no influence on the vibrations of interest in a molecule. The second term of the r.h.s., the linear term, has to be zero, because we assume an equilibrium position in \mathbf{q}_e . The system is in \mathbf{q}_e in a stationary point, which is a minimizer of the potential energy hypersurface. The Hamiltonian is

$$H = -\frac{\hbar^2}{2} g^{kn} \frac{\partial^2}{\partial q^k \partial q^n} + \frac{\hbar^2}{2} g^{kn} \Gamma_{kn}^r \frac{\partial}{\partial q^r} + \frac{\hbar^2}{2} g^{kn} \Gamma_{kr}^r \frac{\partial}{\partial q^n} - \frac{\hbar^2}{8} g^{kn} \Gamma_{kr}^r \Gamma_{ns}^s - \frac{\hbar^2}{4} g^{kn} \Gamma_{kn}^r \Gamma_{rs}^s + \frac{\hbar^2}{4} g^{kn} \frac{\partial \Gamma_{kr}^r}{\partial q^n} + V \quad (3)$$

g^{kn} are the elements of the rank-2 contravariant metric tensor, Γ_{kn}^r are the Christoffel symbols of second kind [11,12]. Not all terms in Eq. (3) are

of the same order. A good approximation of formula (3) is given by

$$H \approx -\frac{\hbar^2}{2} g^{kn} \frac{\partial^2}{\partial q^k \partial q^n} - \frac{\hbar^2}{2} \frac{\partial g^{kn}}{\partial q^k} \frac{\partial}{\partial q^n} + V \quad (4)$$

An harmonic approximation of the kinetic energy means the development of the g_{kn} terms and a cut of the power series expansion, already after the absolute term. Hence, the Hamiltonian in harmonic approximation is

$$H \approx -\frac{\hbar^2}{2} g^{kn}(\mathbf{q}_e) \frac{\partial^2}{\partial q^k \partial q^n} + \frac{1}{2} \frac{\partial^2 V(\mathbf{q}_e)}{\partial q^k \partial q^n} \Delta q^k \Delta q^n \quad (5)$$

Using this harmonic approximation, we can transform to principal axes both, the kinetic energy and, at the same time, also the potential energy [1,13]. The solution of the principal axes problem includes the solution of the eigenvalue problem

$$g^{kn}(\mathbf{q}_e) f_{nr} l_s^r = l_n^k \delta^{nr} \lambda_{rs} \quad (6)$$

f_{nr} are the elements of the force constants matrix in internal coordinates

$$f_{kn} = \frac{\partial^2 V(\mathbf{q}_e)}{\partial q^k \partial q^n} \quad (7)$$

δ^{nr} is the symbol of Kronecker, and λ_{rs} are elements of the matrix of eigenvalues. The internal coordinates are calculated with the matrix \mathbf{L} of eigenvectors and with the curvilinear normal coordinates \mathbf{Q}

$$\Delta q^k = l_n^k Q^n \quad (8)$$

Since the problem is formulated in normal coordinates, then kinetic energy and potential energy are separated, they are decoupled.

The usual understanding of vibrational motions is based on internal coordinates. On the other hand, an animation of molecular vibrations needs a Cartesian representation of trajectories of the involved atoms. To make a computer graphic, we have to compute the screen points. The available screen points are addressed by Cartesian coordinate tupels. The movement of a vibration goes on in a subspace of all possible changes of all atomic positions. Thus, we have to develop a scheme for the subspace of interest. We use developments in power series expansions of the internal

coordinates. These internal coordinates are given themselves by series expansions of powers of mass weighted Cartesian coordinates \tilde{x} .

$$\begin{aligned} \Delta \tilde{x}^a = & \frac{\partial \tilde{x}^a(\mathbf{q}_e)}{\partial q^k} \Delta q^k + \frac{1}{2} \frac{\partial^2 \tilde{x}^a(\mathbf{q}_e)}{\partial q^k \partial q^n} \Delta q^k \Delta q^n \\ & + \frac{1}{6} \frac{\partial^3 \tilde{x}^a(\mathbf{q}_e)}{\partial q^k \partial q^n \partial q^r} \Delta q^k \Delta q^n \Delta q^r + \dots \end{aligned} \quad (9)$$

The differential quotients in series expansion (9) are not directly calculable by derivations. It is necessary to create a new method to develop these differential quotients. The internal coordinates are given in explicit form by functions of the mass weighted Cartesian coordinates, but the inversion of this relation is not given [14]. This gap is caused by the problem of the 6 degrees of freedom of a molecular translation and rotation giving zeros in the inversion matrix. The terms $\partial \tilde{x}^a / \partial q^k$ are the vector base of the interesting subspace. They are calculated with the reciprocal vector base and the covariant metric tensor. Vector base and reciprocal vector base define the orthogonal projector

$$p_a^b = \frac{\partial \tilde{x}^b}{\partial q^k} \frac{\partial q^k}{\partial \tilde{x}^a} \quad (10)$$

From Eq. (10) we can conclude

$$\frac{\partial \tilde{x}^a}{\partial q^k} = \delta^{ab} p_b^c \frac{\partial q^n}{\partial \tilde{x}^c} g_{nk} \quad (11)$$

The summation over index c in Eq. (11) corresponds to the projection of the reciprocal vector base. This projection of the reciprocal vector base is the full reciprocal vector base. From (11) we get the relation

$$\frac{\partial \tilde{x}^a}{\partial q^k} = \delta^{ab} \frac{\partial q^n}{\partial \tilde{x}^b} g_{nk} \quad (12)$$

If we differentiate, we are lead to

$$\frac{\partial^2 \tilde{x}^a}{\partial q^k \partial q^n} = \delta^{ab} \frac{\partial q^r}{\partial \tilde{x}^b} g_{rs} \Gamma_{kn}^s \quad (13)$$

And again, a next differentiation gives

$$\frac{\partial^3 \tilde{x}^a}{\partial q^k \partial q^n \partial q^r} = \delta^{ab} \frac{\partial q^s}{\partial \tilde{x}^b} g_{st} \Gamma_{ru}^t \Gamma_{kn}^u + \delta^{ab} \frac{\partial q^s}{\partial \tilde{x}^b} g_{st} \frac{\partial \Gamma_{kn}^t}{\partial q^r} \quad (14)$$

The differential quotients in Eq. (9) are given by

Eqs. (12) to (14). The Christoffel symbols of second kind are

$$\Gamma_{kn}^r = -g_{ks} \frac{\partial q^s}{\partial \tilde{x}^a} \delta^{ab} \frac{\partial^2 q^r}{\partial \tilde{x}^b \partial \tilde{x}^c} \delta^{cd} \frac{\partial q^l}{\partial \tilde{x}^d} g_{lm} \quad (15)$$

Their derivatives are given by

$$\begin{aligned} \frac{\partial \Gamma_{kn}^r}{\partial q^s} &= \Gamma_{kt}^r \Gamma_{ns}^t + \Gamma_{nt}^r \Gamma_{ks}^t - \frac{\partial^3 q^r}{\partial \tilde{x}^a \partial \tilde{x}^b \partial \tilde{x}^c} \delta^{ad} \\ &\times \frac{\partial q^l}{\partial \tilde{x}^d} g_{lk} \delta^{be} \frac{\partial q^u}{\partial \tilde{x}^e} g_{un} \delta^{cf} \frac{\partial q^v}{\partial \tilde{x}^f} g_{vs} \end{aligned} \quad (16)$$

The detour from mass weighted Cartesian coordinates [15] to Cartesian coordinates via internal coordinates gives a power series expansions, which is a Cartesian representation of the curvilinear trajectories of the atoms

$$\begin{aligned} \Delta x^a &= m^{ab} \frac{\partial q^n(\mathbf{x}_e)}{\partial x^b} g_{nk}(\mathbf{q}_e) \Delta q^k \\ &+ \frac{1}{2} m^{ab} \frac{\partial^2 q^r(\mathbf{x}_e)}{\partial x^b} g_{rs}(\mathbf{q}_e) \Gamma_{kn}^s(\mathbf{q}_e) \Delta q^k \Delta q^n \\ &+ \frac{1}{6} \left[m^{ab} \frac{\partial^3 q^s(\mathbf{x}_e)}{\partial x^b} g_{st}(\mathbf{q}_e) \Gamma_{ru}^t(\mathbf{q}_e) \Gamma_{kn}^u(\mathbf{q}_e) \right. \\ &\left. + m^{ab} \frac{\partial^2 q^s(\mathbf{x}_e)}{\partial x^b} g_{st}(\mathbf{q}_e) \frac{\partial \Gamma_{kn}^t(\mathbf{q}_e)}{\partial q^r} \right] \\ &\times \Delta q^k \Delta q^n \Delta q^r + \dots \end{aligned} \quad (17)$$

m^{ab} are the elements of the inverse mass matrix being a diagonal matrix. In Eqs. (15) and (16), there the elements of the inverse mass matrix are represented in explicit form.

$$\Gamma_{kn}^r = -g_{ks} \frac{\partial q^s}{\partial x^a} m^{ab} \frac{\partial^2 q^r}{\partial x^b \partial x^c} m^{cd} \frac{\partial q^l}{\partial x^d} g_{lm} \quad (18)$$

$$\begin{aligned} \frac{\partial \Gamma_{kn}^r}{\partial q^s} &= \Gamma_{kt}^r \Gamma_{ns}^t + \Gamma_{nt}^r \Gamma_{ks}^t - \frac{\partial^3 q^r}{\partial x^a \partial x^b \partial x^c} m^{ad} \\ &\times \frac{\partial q^l}{\partial x^d} g_{lk} m^{be} \frac{\partial q^u}{\partial x^e} g_{un} m^{cf} \frac{\partial q^v}{\partial x^f} g_{vs} \end{aligned} \quad (19)$$

The elements of the contravariant metric tensor are

$$g^{kn} = \frac{\partial q^k}{\partial x^a} m^{ab} \frac{\partial q^n}{\partial x^b} \quad (20)$$

Thus, the problem is reduced to the calculation of derivatives of internal coordinates to Cartesian coordinates.

We have written program GF in FORTRAN 77 [16]. It calculates the trajectories of atoms as a data file of Cartesian coordinate tupels for an animation program.

3. A consideration of molecular vibrations in the theory of molecular modelling

The geometrical measurement of a molecule in the equilibrium state is changed by vibrations. Generally, the extension of a molecule is greater than the geometry of the equilibrium state. For molecular modelling [8], the problem is important, which space the molecule needs in the course of its vibration.

For a calculation of the space needed under vibrations, we calculate for every normal coordinate the mean value

$$\mu^k = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \Psi_n^* Q^k \Psi_n \prod_r dQ^r \quad (21)$$

and the dispersion

$$D^k = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \Psi_n^* (Q^k - \mu^k) \Psi_n \prod_r dQ^r \quad (22)$$

The eigenfunctions Ψ_n are products of eigenfunctions of the harmonic oscillator. The integrals (21) and (22) are fully integrable; the solutions are:

$$\mu^k = 0, \quad D^k = \frac{(2n_k + 1)\hbar}{2\sqrt{\lambda_{kk}}} \quad (23)$$

n_k is the quantum number of the vibration and λ_{kk} is the eigenvalue of normal vibration k . With (23) we can calculate the ranges of the normal coordinates

$$\mathcal{Q}_{-1}^k = - \left[\sum_r D^r \right]^{1/2}, \quad \mathcal{Q}_{+1}^k = + \left[\sum_r D^r \right]^{1/2} \quad (24)$$

If the normal vibration k is twofold degenerated, then the sums in (24) have two terms correspondingly, the dispersions of the normal coordinates, which describe this vibration. Analogously, in cases of higher degeneracy, we have more terms.

If we have the ranges of normal coordinates, we can compute the range of internal coordinates

using relation (8)

$$\Delta q_{-1}^k = \sum_r l_r^k \mathcal{D}_{sgn(-l_r^k)}^r, \quad \Delta q_{+1}^k = \sum_r l_r^k \mathcal{D}_{sgn(l_r^k)}^r \quad (25)$$

The visual representation in space of the full range of the vibrating molecule makes it necessary to overlay the representations of the molecule in different geometries, given by the points

$$\Delta q^k = \frac{r_k - s_k + 1}{r_k} \Delta q_{-1}^k + \frac{s_k - 1}{r_k} \Delta q_{+1}^k, \quad s_k = 1, \dots, r_{k+1} \quad (26)$$

The quality of a representation depends strongly on the number of the r_k . Over all, there are to compute, and also to represent, $\prod_k (r_k + 1)$ geometries using Eq. (17).

4. The computer programs

Calculation and visualisation of molecular vibrations have considerable complexity. Separating calculation from visualisation, visualisation can be done even with medium hardware capabilities. The following steps must be taken:

- (i) Computation of data of the molecule: cartesian coordinates of the atoms, internal coordinates, Cartesian force constants, . . . These calculations can be done by GAUSSIAN 80, MNDO or other well known programs.
- (ii) The output of the first step provides the input of our program GF calculating the molecular vibrations. GF provides
 - information about the normal mode of the molecules
 - Cartesian coordinates of all atoms during one period of the vibration, which represent the trajectories of the atoms
 - two corresponding quantum numbers
 - GF is compiled from a FORTRAN 77-source.
- (iii) The output of step-2-calculations contain all data needed for visualization. Its volume is considerable. It is contained in seven files. Our goal was also to enable visualization on a IBM-compatible PC. In order to handle

these datafiles by a program running under a DOS-like operating system with its strongly limited resources, the datafiles are converted to a direct-access-file by the programm EINAUS.EXE. On UNIX operating system computers the output files of GF are handled directly. Here visualisation makes profit from graphical hardware. We used a SGI computer with its GL-library. The visualisation-software SHOWVIB also can be compiled on other systems using this library. The used method is ray-tracing.

All software including sources, comments on the structure of datafiles in detail and examples is contained in the file ANIVIB.TAR.Z (directory: /PUB/UNI-LEIPZIG) available via anonymous ftp from the ftp-server of the Leipzig University (SERVER2.RZ.UNI-LEIPZIG.DE).

5. The program GF

We have developed the FORTRAN 77 program GF [16]. The name GF is a tribute to the famous Wilson GF matrix theory [13]. It realizes the interface between program systems of molecular physics, quantum chemistry and an animation program [17]. Fig. 1 shows the structure of the program GF. The input for the program includes data about the molecule, like atomic numbers and Cartesian coordinates of the atoms. Further input are the internal coordinates. The concept of the program allows any linear combination of internal coordinates. Thus, it is possible to define symmetry coordinates [18] or Pulay's coordinates [19]. The last input is the matrix of Cartesian force constants.

The program transforms the matrix of force constants in the defined internal coordinates. The next step is the solution of the eigenvalue problem of the harmonic vibrational analysis (6) using a Cholevsky factorization [20] of the covariant metric tensor. Trajectories of atoms corresponding to Eq. (8) are computed, where the used coordinates are the internal ones. But, the animation of molecular vibration makes it necessary to represent these trajectories in Cartesian coordinates. The

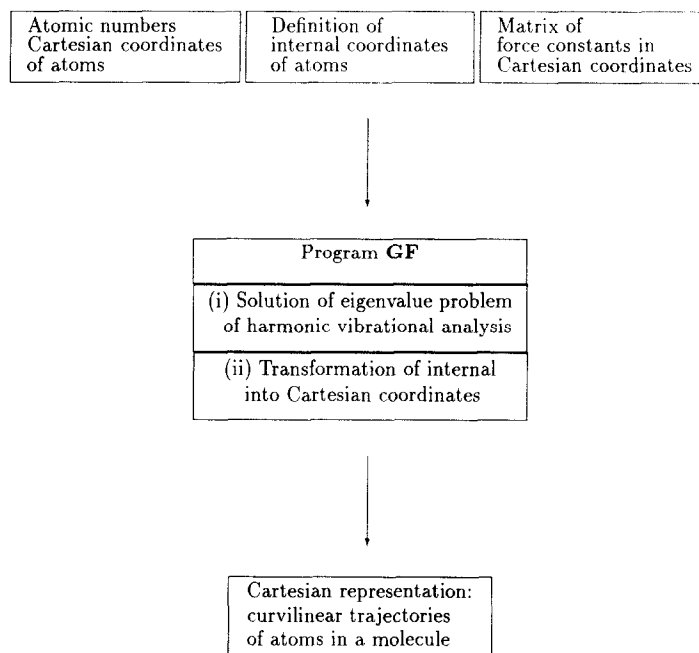


Fig. 1. Structure of the program GF.

program computes with Eq. (17) Cartesian coordinates from the internal coordinates. This version of the program does this step up to linear and quadratic terms of the power series expansion; and it gets the trajectories of atoms as a tuple of Cartesian coordinates for the animation. The representation of the trajectories does also depend on quantum numbers of the vibrational state. The trajectory of a nondegenerate normal vibration only depends on one quantum number. Trajectories of atoms of degenerated normal vibrations are defined by two quantum numbers [21].

Output of program GF is stored in a five-dimensional field

$DXYZ(INDEX1, INDEX2, INDEX3, INDEX4, INDEX5)$

The first INDEX1 describes normal modes of the molecule. This can be nondegenerate or degenerate normal vibrations. With this definition, for example, the ethane molecule has 6 nondegenerate and 6 twofold degenerate normal modes. The second INDEX2 describes the Cartesian coordinates. INDEX3 contains the course of any Cartesian coordinate for one period of the corresponding

normal vibration. INDEX4 and INDEX5 are quantum numbers. In case of a nondegenerate normal vibration, there is only one quantum number of relevance [12], and INDEX5 is meaningless. The field DXYZ contains all data for an animation program, in our laboratory the program ANIVIB [17]. Additionally, program GF calculates the structure of the molecule. The first program ANIVIB was a 32-bit version on PC level, and it is now available for work stations (IBM-RISC/6000, Silicon Graphics Indigo).

In Fig. 2 we give as an example the molecule ethane, in three different snapshots, in the torsional vibration at 182.4 (A_{1g}) in the first row, in the deformation vibration at 1478.7 (A_{2u}) in the second row, and in the deformation vibration at 1498.7 (A_{1g}) in the lower row.

6. Discussion

We note that this program deals only with the vibration of a molecule in its internal coordinates. These have to be defined in an adequate form. In general, a large amplitude vibration of a molecule

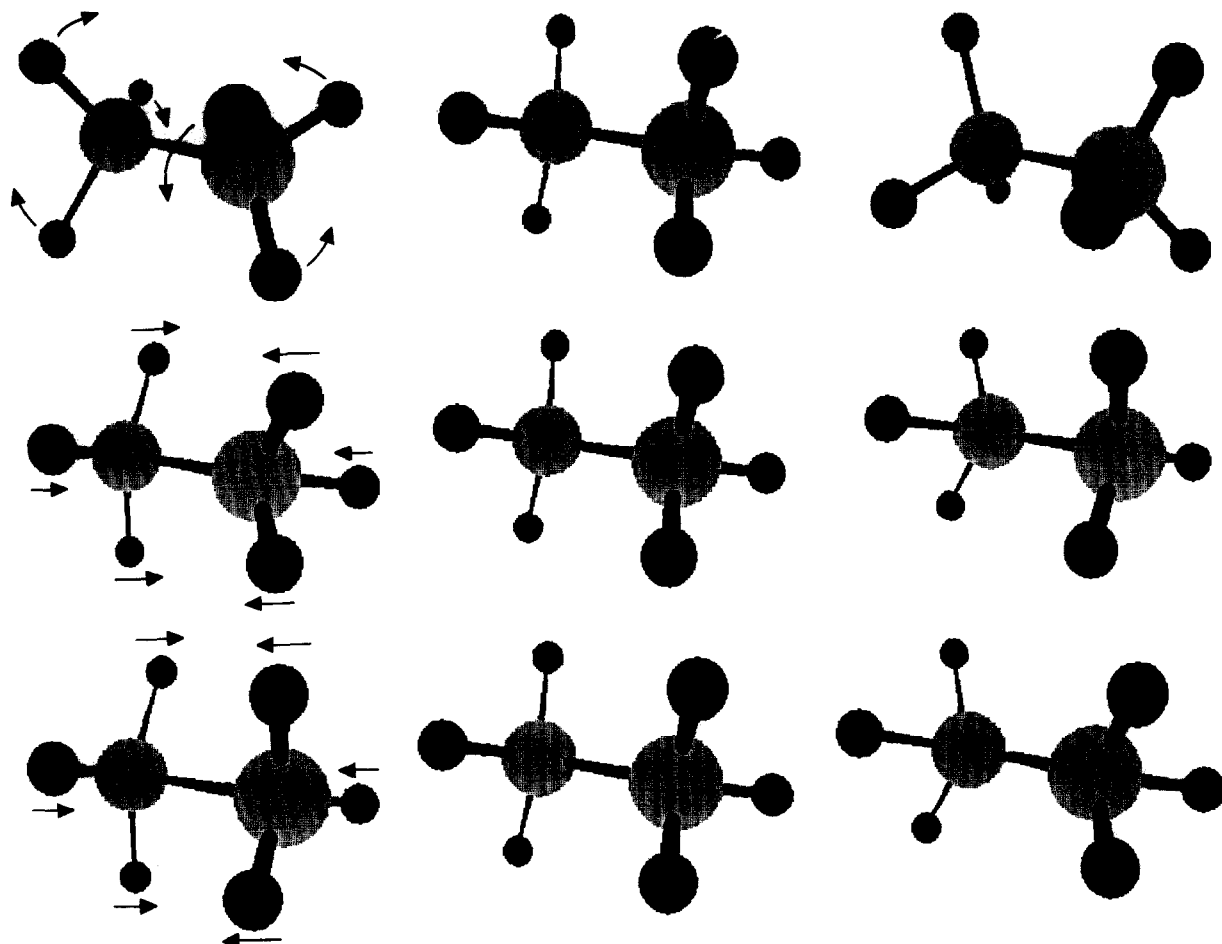


Fig. 2. Torsion in the first row, and deformation vibrations of the ethane molecule (screen dumps of snapshots). The center column shows the equilibrium. (You should see it in color and in motion!)

strongly depends on the shape of the potential energy hypersurface [22]. The advantage of internal coordinates is to meet better the global path of a curvilinear potential valley than the Cartesian normal coordinates [23]. The relationship between potential energy surface valleys and internal coordinates is a new problem, cf. [14,24].

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