Accurate Numerical Computation of Rovibrational G Matrices in Molecules of Arbitrary Size

María Eugenia Castro, Alfonso Niño, and Camelia Muñoz-Caro

Grupo de Química Computacional y Computación de Alto Rendimiento
Escuela Superior de Informática. Universidad de Castilla-La Mancha
Paseo de la Universidad 4, 13071 Ciudad Real, Spain
{mariaeugenia.castro,alfonso.nino,camelia.munoz}@uclm.es

Abstract. In this work we present a methodology for the accurate numerical computation of the rovibrational G matrix in any molecule. A C++ program is developed to apply this methodology. Using polymorphism, the program can handle the output of any of the available electronic structure codes. The objective is to compute the kinetic contribution to the rovibrational Hamiltonian from the results of molecular structure scans, performed in heterogeneous and distributed systems such as Internet-based Grids of computers. The numerical derivatives needed to compute the G matrix in curvilinear, internal coordinates are obtained from an adapted Richardson extrapolation. The procedure is optimized to maximize the number of significant digits in the derivatives. Using the program, we compute the vibrational kinetic terms for several simultaneous torsional motions in Glycolaldehyde, Methyl formate and Ethyl methyl ether. The results show the existence of an important coupling among the torsional vibration modes.

Keywords: G matrix, Kinetic operator, Numerical differentiation, Richardson extrapolation.

1 Introduction

Some typical numerical operations (differentiation, integration, interpolation…) can be implemented in robust algorithms in order to become more efficient for the resolution of physical or chemical problems. As an example, we have the studies related to the calculation of vibrational contributions, spectroscopic data, anharmonic effects, or vibrational spectra. In particular, the usefulness of numerical differentiation methods in the construction of rovibrational Hamiltonians is apparent. In this context, several theoretical works have resorted to numerical evaluations of the kinetic energy operator, due to the complexity of analytical expressions in large systems or in problems taking into account several coupled vibrational coordinates. Most of these works deal with systems depending on large amplitude vibrational motions: one-dimensional studies of ring puckering in four-membered rings [1, 2], methyl torsion in methanol [3] and 2-methylpropanal [4], inversion of ammonia [5, 6], and bending in triatomic molecules [4, 7]. Also two-dimensional studies have been carried out on several

species such as the methyl + aldehydic torsions in propanal [8], the OH torsion + NH_2 wagging in hydroxylamine [9], the rotation + torsion of protonated methane [10], the methyl + phosphine torsions in ethylphosphine [11], or the methyl torsion + aldehydic hydrogen wagging of acetaldehyde [5, 12, 13] and acetone [12]. Additionally, three-dimensional studies have been performed on, for instance, the two methyl torsions + bending in dimethylamine [14], the methyl torsion + aldehydic hydrogen wagging + CCO bending in acetaldehyde [15], or the OH torsion + NH_2 inversion + NH_2 twist in hydroxylamine [16]. Models using up to five-dimensional normal modes as coordinates have been employed for the interpretation of the vibrational spectrum of this last molecule [16]. In a different work, a six-dimensional study of the inversion dynamics of ammonia and of the vibrational dynamics of H_2O_2 has been reported [17].

Some of the previous works [1, 2, 4, 9, 16, 17] are based in the early theoretical studies of Meyer [18, 19]. This author developed a numerical treatment of internal motions in one and two dimensions, for non-linear molecules, as a tool to interpret spectroscopic molecular data. His numerical methods include a representation of a grid of points based in a trigonometric interpolation, and an iterative technique for calculating eigenvectors. Other works [3, 4-6, 8, 11-14] are based in the methodology developed by Harthcock and Laane [20, 21]. These authors published a general development of the vibrational Hamiltonian. Here, the determination of the kinetic terms includes the numerical calculation of the derivatives of nuclear positions respect to the vibrational coordinates. Finite differences are used. In fact, all the mentioned works use numerical differentiation for the calculation of the derivatives required to build the kinetic energy operator in the vibrational Hamiltonian.

On the other hand, some numerical methods for computing the derivatives involved in the kinetic operator have been implemented in different software tools [2, 4, 6, 10, 12, 13]. Thus, Niño and Muñoz-Caro [12] developed a program for the calculation of the rotational-vibrational G matrix [22]. The program computes the derivatives of the nuclear positions with respect to the vibrational coordinates by central finite differences. Using an empirical approach, appropriate increments of the vibrational coordinates needed for the numerical derivatives are proposed. Makarewicz [2] presented a program to solve the rovibrational problem for large amplitude vibrational motions. In this program, the calculation of the derivatives of the nuclear positions is defined by the user in a separate subroutine. The derivatives are numerically calculated from third to sixth order interpolation formulas. In turn, Rush and Wiberg [6] developed FORTRAN programs [23] for evaluating the numerical solution of the one-dimensional Schrödinger equation using the Numerov-Cooley algorithm [24]. Here, the partial derivatives involved in the G matrix were approximated numerically by finite differences. East and Bunker [10] presented a general computer program to compute rotation-contortion energy levels for molecules having one large amplitude vibrational degree of freedom. In that work the authors suggested that the boundary conditions in the numerical differentiation part of the program must be chosen appropriately. Boundary conditions for the Numerov-Cooley algorithm [24] are in a separate subroutine.

More recently, Lauvergnat and Nauts [4] developed an algorithm for computing the molecular kinetic operator in curvilinear coordinates. In this program [25], the calculation of the Cartesian coordinate derivatives with respect to the internal coordinates, and the derivatives of the inertia tensor, Coriolis, deformation and rovibrational

matrices are numerically evaluated. The derivatives are calculated without resorting to finite difference schemes. Rather, these computations are based on a numerical procedure resorting to a Gaussian elimination. The procedure is described in the framework of the dimensionality reduction [1, 6-9, 11, 21, 26].

In this work, we present a methodology for the construction of reliable kinetic terms for anharmonic vibrational Hamiltonians in molecules of arbitrary complexity. Thus, we develop and implement accurate numerical differentiation algorithms for the computation of the kinetic terms in the framework of the rovibrational G matrix. A software system is designed to apply this methodology to the large sets of molecular structures generated in the previously described [27] mapping of potential energy hypersurfaces in computational Grid environments. Vibrational motions described by curvilinear, internal coordinates are considered.

2 Methodology

The general (anharmonic) rovibrational Hamiltonian for an arbitrary non-linear molecular system with N atoms is given by [13, 21, 28]:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \left[g_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \left(\frac{\partial g_{ij}}{\partial q_i}\right) \frac{\partial}{\partial q_j} \right] + V(q_1, \ldots, q_{3N-6}) \cdot \tag{1}$$

where the q_i's represent arbitrary vibrational coordinates, the g_{ij} are the elements of the rovibrational G matrix, and V is the potential function, which depends on the q_i's coordinates. In Equation (1) the first term represents the kinetic contribution. In turn, the rovibrational G matrix is defined as [21]:

$$G = \begin{pmatrix} I & X \\ X^T & Y \end{pmatrix}^{-1} . \tag{2}$$

Here, I represents the inertia tensor, *i.e.*, the overall rotation contribution, Y corresponds to the pure vibration contribution, and X represents the vibration-rotation interaction (Coriolis terms). The elements of I, X and Y are obtained from the molecular structure as,

$$I_{ii} = \sum_{\alpha}^{N} m_{\alpha} \left[(r_{\alpha})^2 - (r_{\alpha i})^2 \right] , \quad I_{ij} = -\sum_{\alpha}^{N} m_{\alpha} r_{\alpha i} r_{\alpha j}$$

$$X_{ij} = \sum_{\alpha}^{N} m_{\alpha} \left[r_{\alpha} \times \left(\frac{\partial r_{\alpha}}{\partial q_i}\right) \right]_j \tag{3}$$

$$Y_{ij} = \sum_{\alpha}^{N} m_{\alpha} \left(\frac{\partial r_{\alpha}}{\partial q_i}\right) \cdot \left(\frac{\partial r_{\alpha}}{\partial q_j}\right) .$$

where the α index runs on the number of atoms in the molecule.

The key point in the above treatment is the computation of the G matrix. Equation (3) shows that for such a goal, derivatives of the nuclear coordinates with respect to the vibrational coordinates are needed. In the general case, with arbitrary vibrational coordinates, analytical computation of these derivatives can be complicated and hardly generalizable. A more general approach is to resort to numerical computations [4, 7] as long as the accuracy of the resulting data is known and appropriate for the problem at hand. Let us consider this problem.

The derivatives of the nuclear positions with respect to the vibrational coordinates appearing in Equation (3) can be initially calculated by central finite differences. To such an end, we consider for each vibrational coordinate an arbitrary increment Δq_i. Thus, applying a Taylor expansion we have,

$$r_{\alpha j}(q_i + \Delta q_i) = r_{\alpha j}(q_i) + \Delta q_i \frac{\partial r_{\alpha j}(q_i)}{\partial q_i} + \frac{1}{2} \Delta q_i^2 \frac{\partial^2 r_{\alpha j}(q_i)}{\partial q_i^2}$$
$$+ \frac{1}{6} \Delta q_i^3 \frac{\partial^3 r_{\alpha j}(q_i)}{\partial q_i^3} + \cdots$$

$$r_{\alpha j}(q_i - \Delta q_i) = r_{\alpha j}(q_i) - \Delta q_i \frac{\partial r_{\alpha j}(q_i)}{\partial q_i} + \frac{1}{2} \Delta q_i^2 \frac{\partial^2 r_{\alpha j}(q_i)}{\partial q_i^2}$$
$$- \frac{1}{6} \Delta q_i^3 \frac{\partial^3 r_{\alpha j}(q_i)}{\partial q_i^3} + \cdots$$

(4)

where the j index represents one of the three Cartesian coordinates. Subtracting the above expressions and rearranging, an estimation of the first derivative is obtained

$$\frac{\partial r_{\alpha j}(q_i)}{\partial q_i} = \frac{r_{\alpha j}(q_i + \Delta q_i) - r_{\alpha j}(q_i - \Delta q_i)}{2\Delta q_i} + \frac{1}{3!} \Delta q_i^2 \frac{\partial^3 r_{\alpha j}(q_i)}{\partial q_i^3}$$
$$+ \frac{1}{5!} \Delta q_i^4 \frac{\partial^5 r_{\alpha j}(q_i)}{\partial q_i^5} + \cdots$$

(5)

Approaching the derivative by the first term to the right of the equal sign, we get

$$\frac{\partial r_{\alpha j}(q_i)}{\partial q_i} \cong \frac{r_{\alpha j}(q_i + \Delta q_i) - r_{\alpha j}(q_i - \Delta q_i)}{2\Delta q_i} .$$

(6)

The truncation error in equation (6) is of order $O(\Delta q_i^2)$. To obtain accurate results for the numerical derivatives, an appropriate value for the Δq_i increment must be used. This can be accomplished in the following way. Two errors affect equation (6): truncation and roundoff error. The truncation error, ε_t, comes from neglecting terms higher than the second in the Taylor series expansions of equation (4). In our case,

$$\varepsilon_t \cong \Delta q_i^2 \cdot \frac{\partial^3 r_{\alpha j}(q_i)}{\partial q_i^3} \cdot \tag{7}$$

On the other hand, the order of the roundoff error, ε_r, in equation (6) can be estimated using floating point arithmetic. Thus, we have [29],

$$\varepsilon_r \cong \varepsilon_f \left| \frac{r_{\alpha j}(q_i)}{\Delta q_i} \right| \cdot \tag{8}$$

Here ε_f is the fractional accuracy with which $r_{\alpha j}(q_i)$ is computed. This value is at least equal to the machine epsilon (the machine precision). So, in a first approach we have $\varepsilon_f \approx \varepsilon_m$. The ε_m for a floating point value in double precision using the IEEE 754 standard representation is about 10^{-16} [30].

With the above considerations, the total error associated to equation (6) can be obtained as $\varepsilon_t + \varepsilon_r$. Minimizing this error with respect to Δq_i we obtain the optimal increment:

$$\Delta q_i = \left[\varepsilon_f \ \frac{r_{\alpha j}(q_i)}{(\partial^3 r_{\alpha j}(q_i)/\partial q_i^3)} \right]^{1/3} \cdot \tag{9}$$

This result represents the best increment of vibrational coordinates that can be used to compute, by central finite differences, the derivatives needed for the rovibrational G matrix, see equation (3). However, equation (3) shows that a total of $3N$ derivatives is needed, one for each nuclear Cartesian coordinate. Considering the set of $3N$ derivatives, we can compute an overall optimal increment as the square root of the quadratic average. So, the optimal Δq overall increment (which will be called the step size, h) would be

$$h = \left[\sum_i^N \sum_j^3 \left[3\varepsilon_f \cdot \frac{r_{\alpha j}(q_i)}{(\partial^3 r_{\alpha j}(q_i)/\partial q_i^3)} \right]^{2/3} \bigg/ 3N \right]^{1/2} \cdot \tag{10}$$

The expression for the third numerical derivative needed in equation (10) can be numerically determined from Taylor expansions similar to those of equation (4). Thus, using increments of Δq_i and $2\Delta q_i$ we get:

$$\partial^3 r_\alpha(q_{ij})/\partial q_{ij}^3 \cong \left[r_\alpha\left(q_{ij} + 2\Delta q_{ij}\right) - r_\alpha\left(q_{ij} - 2\Delta q_{ij}\right) - 2r_\alpha\left(q_{ij} + 2\Delta q_{ij}\right) \right.$$
$$\left. - 2r_\alpha\left(q_{ij} - 2\Delta q_{ij}\right) \right] \bigg/ 2\Delta q_{ij}^3 \cdot \tag{11}$$

The truncation error is of order $O(\Delta q_i^2)$ as in equation (6). So, no loss of accuracy is associated to the use of equation (11) for the third derivative.

Given an appropriate step size, h, the accuracy of the obtained derivative can be increased by using Richardson extrapolation [31]. We can use this technique in the following form. Equation (5) can be rewritten as

$$\frac{\partial r_{\alpha j}(q_i)}{\partial q_i} = D(h) + A h^2 + B h^4 + \cdots \tag{12}$$

where $D(h)$ represents the approximate derivative given by equation (6) using a step size h. Using two different step sizes, h_0 and h_1, we can build a system of two equations and obtain A. Including the $A h^2$ term we get a better approach to the first derivative, with an error reduced from $O(h^2)$ to $O(h^4)$. Repetition of the procedure with a different step size permits to obtain B. In this form, the error reduces to $O(h^6)$. Successive application of the technique permits to obtain better approximations to the derivative. Usually, the sequence of step size values is given by (h, $h/2$, $h/4$…). In this case, we obtain the following recurrence relation between two applications of the extrapolation, i and $i+1$

$$D_{i+1}(h) \cong \frac{2^{2(i+1)} D_i(h/2) - D_i(h)}{2^{2(i+1)} - 1}. \tag{13}$$

with error $O(h^{2(i+2)})$. An estimation of the error in the derivative can be obtained as the difference between the two last values computed in the procedure.

We have implemented this methodology on our software tool and it has been calibrated using three test molecules as described in section 4.

3 Program Description

The previous methodology has been implemented in a C++ program. C++ has been selected because, apart from being an efficient language, it has useful object oriented characteristics such as encapsulation, inheritance and polymorphism [32]. The program is intended to compute the G matrix elements from the structural results of potential energy hypersurface mappings obtained in computational Grid environments [27]. These mappings can be obtained using the available standard electronic structure codes. The program is organized in two components: the functional and interface parts. The functional part is responsible for the computation of the G matrix elements. The interface part is responsible for the acquisition of data from any of the formats used by the electronic structure programs. We will describe briefly each component

Figure 1 shows the classes and their relationships through an UML class diagram. UML (Unified Modeling Language) [33] is a graphical language allowing the design of object-oriented software systems using a standard notation. Figure 1 shows that the method *main* (the starting point of the program) belongs formally to the Kinetic class. As it is shown by the continuous line in Figure 1, the MolecularData class is used by the Kinetic class. MolecularData is used to get the molecular structure from the results of electronic structure computations. The behaviour of this class is later detailed. The functional part is structured in five classes. The Gmatrix class contains and handles all the information about the rovibrational G matrix. This is an abstract class used

to define the public interface of functions that all its descendent classes must implement. The GmatrixZ class extends Gmatrix by inheritance and contains the information of the G matrix in arbitrary internal coordinates. In this class the inertial tensor, I matrix, is computed, as well as the rotation-vibration interaction X matrix, and the vibrational Y matrix, see equation (3). This class has the necessary methods to obtain center of mass and principal axis coordinates. This class implements the methodology developed in section 2 for computing accurate numerical derivatives. GmatrixQ extends Gmatrix by inheritance, allowing for the use of normal modes as vibrational coordinates. This class is not yet implemented. The Structure class contains and handles the general information of a molecular system like number of atoms, atomic numbers, Cartesian coordinates, etc. The continuous line in Figure 1 shows that this class is used by GmatrixQ. The Zmat class contains the definition and values of the internal coordinates. This class also contains the methods for converting to internal from cartesian coordinates, and to cartesian from internal coordinates. Zmat exhibits an inheritance relationship with Structure and is used by GmatrixZ, see Figure 1.
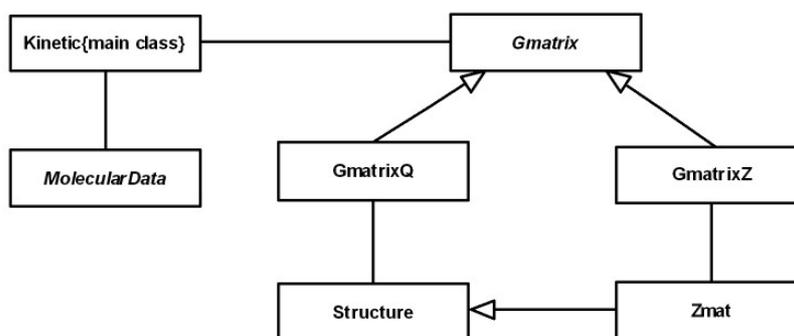

Fig. 1. UML class diagram for the program

The interface part of the program resorts to polymorphism for handling in a unified way the different data formats found in the standard electronic structure codes. In object orientation polymorphism is the ability of objects of different classes to respond to method (function) calls of the same name [34]. To such an end an inheritance relationship is needed. Then, a reference to an object of father class can be used to refer to any object of a descendant class. Figure 2 shows an UML class diagram corresponding to the interface part of the program. The MolecularData class is the father (abstract) class that defines the reading data methods. This class makes use of the information (atomic masses and symbols) contained in the AtomicData package. Their derived classes contain the specific code for reading from each specific electronic structure package: GaussianMolecularData for Gaussian [35], GamessMolecularData for Gamess [36], MolproMolecularData for Molpro [37], or DaltonMolecularData for Dalton [38]. At present, the GaussianMolecularData, and GamessMolecularData classes are available.
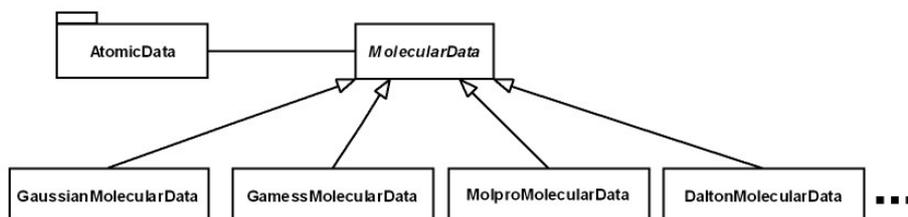
Fig. 2. UML class diagram of the interface part of the program

4   Results and Discussion

4.1   Calibration Molecular Set

The different parameters used in the methodology described in section 2 are calibrated using a set of molecules. We select three floppy molecules of astrophysical interest and different sizes: Glycolaldehyde [39], Methyl formate [40] and Ethyl methyl ether [41]. Figure 3 collects the structures and numbering conventions used here for these molecules. In the three cases, fully relaxed molecular structures, for the most stable conformations in the ground electronic state, are computed using *ab initio* methodology. In these calculations, correlation energy is accounted for at the MP2 level [42]. As basis set, we used the correlation consistent quadruple-zeta cc-pVQZ basis set [43]. This polarized basis set includes by definition up to *f* functions on hydrogens and up to *g* functions on heavy atoms. All the calculations are carried out
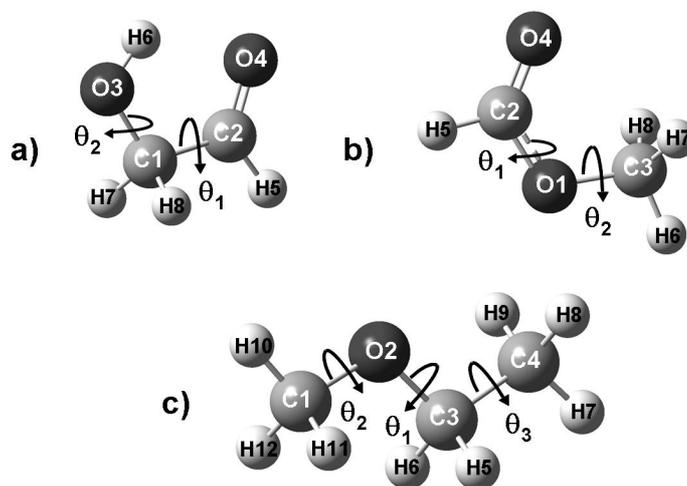

Fig. 3. Molecular structure and numbering convention for *a)* Glycolaldehyde, *b)* Methyl formate and *c)* Ethyl methyl ether. The dihedral angles describing the anharmonic, large amplitude vibrations in the molecules are also included.

with the Gaussian03 package [35]. Several torsional vibrational motions are present in these molecules, as shown in Figure 3. The corresponding vibrational coordinates are defined by dihedral angles as follows. The torsional motions in Glycolaldehyde are described through the θ_1(O4C2C1O3) and θ_2 (H6O3C1C2) angles. In Methyl formate, torsional motions are described by dihedrals θ_1(O4C2O1C3) and θ_2(H6C3O1C2). Finally, in the Ethyl methyl ether the θ_1(H7C4C3O2), θ_2(C4C3O2C1), and θ_3(H10C1O2C3) dihedrals are used.

4.2 Optimal Step Size, h

The optimal step size, h, as defined by equation (10), is determined using the three previous molecules for the three types of internal, curvilinear, coordinates: interatomic distances, valence angles and dihedral angles. For distances and valence angles we have chosen representative parameters, see Table 1. For dihedral angles we use the internal coordinates for torsional motions above defined. As initial increments, h, for

Table 1. Optimal step sizes (h) for numerical computation of derivatives using internal coordinates in Glycolaldehyde, Methyl formate and Ethyl methyl ether. Distances are in Angstroms and angles in degrees.

Parameter	Glycolaldehyde	Methyl Formate	*t*-Ethyl methyl ether
C-C	3.20070E-05	—	2.54397E-05
C=O	3.21368E-05	3.30891E-05	—
C-O	3.18239E-05	3.27263E-05 3.25139E-05	2.80591E-05 2.53679E-05
O-H	3.19844E-05	—	—
C-H	3.20023E-05 3.19669E-05	3.27239E-05 3.27470E-05	2.82855E-05 2.82550E-05
C-C-O	5.76818E-08	—	4.06724E-08
C-O-C	—	5.78759E-08	6.79843E-08
O-C-H	—	6.03496E-08 5.57502E-08	6.49523E-08 5.49151E-08
C-C-H	6.05548E-08 6.09595E-08	—	4.45177E-08
H-C-H	—	6.48551E-08 6.22888E-08	4.35942E-08 4.26554E-08
O=C-C-O	5.58630E-08(θ_1)	—	—
H-O-C-C	5.58801 E-08(θ_2)	—	—
H-C-C-O	5.90919E-08	—	4.39322E-08(θ_1)
O=C-O-C	—	5.71133E-08(θ_1)	—
H-C-O-C	—	6.00067E-08(θ_2)	5.29925E-08(θ_3) 5.05834E-08
C-C-O-C	—	—	4.74542E-08(θ_2)

application of equation (10) we used the values proposed in a previous work: 10^{-2} Å for distances and 10^{-3} degrees for angles [12]. The optimal h values obtained for each parameter are collected in Table 1.

Table 1 shows that for bond lengths the computed h values are very close in all cases. The value is close to 10^{-5} Å. For valence and dihedral angles, we observe again that the optimal increment is similar in all cases. Now the value is close to 10^{-7} degrees. It is well recognized that Richardson extrapolation should begin with step sizes larger than optimal. On the other hand, step sizes smaller than the optimal found here would yield bad estimations. Therefore, these step sizes define the lower limits of coordinate increments that can be used in the Richardson extrapolation.

4.3 Numerical Derivatives by Richardson Extrapolation

Once optimal increments for the different internal coordinates are known we must calibrate Richardson Extrapolation. The target is to determine the optimal couple step size + number of Richardson extrapolations. The main restriction is that the step size used in the higher order extrapolations must not be smaller than the lower limit values determined in the previous section. Many different combinations of step sizes and Richardson extrapolations fulfill this condition. Thus, if h_l represents the limit step size, h the initial step size y n the number of Richardson extrapolations we have

$$h_l = h/2^n . \tag{14}$$

In equation (14) different valid combinations of h and n are possible. To find an optimal combination, we need to choose an h and n value that minimizes the error (ε) in the procedure. As error we propose an index measuring the overall difference among two successive applications of the Richardson extrapolation. This index has the advantage of being related to the number of significant digits, as shown below. To define the index, we use an approach similar to that applied in Equation (10), defining the error index for a whole set of m internal coordinates as,

$$\varepsilon = \left[\sum_k^m \sum_i^N \sum_j^3 \left[D_{ik}\left(h/2\right) - D_{ik}\left(h\right) \right]^2 \Big/ \left[3N\,m \right] \right]^{1/2} . \tag{15}$$

To analyse the variation of the error as a function of h and n we define a grid of points for different h and n values. For distances we use h values between 10^{-1} and 10^{-5} Å. For angles, values between 10^{-3} and 10^{-7} degrees are considered. In both cases n ranges from 1 to 9 Richardson extrapolations. The three calibration molecules, see Figure 3, are used. The results show that the error computed for distances, on one side, and angles, on the other, are almost identical in the three molecules. Thus, we present the results just for one of them. Figure 4 shows the variation of the error in the derivatives as a function of h and n in Glycolaldehyde. To handle more significant values, the minus decimal logarithms of h and the error are used. As from the data in Table 1, we observe that valence and dihedral angles behave similarly. Using Figure 4 we select appropriate combinations of h and n. First, we select h values small in comparison with the usual values of the corresponding internal coordinate. Second we try to minimize the error. Thus, we choose values of $h=10^{-2}$ Å and $n=9$ for distances. For valence and dihedral angles we select as optimal combination, $h=10^{-4}$ degrees and
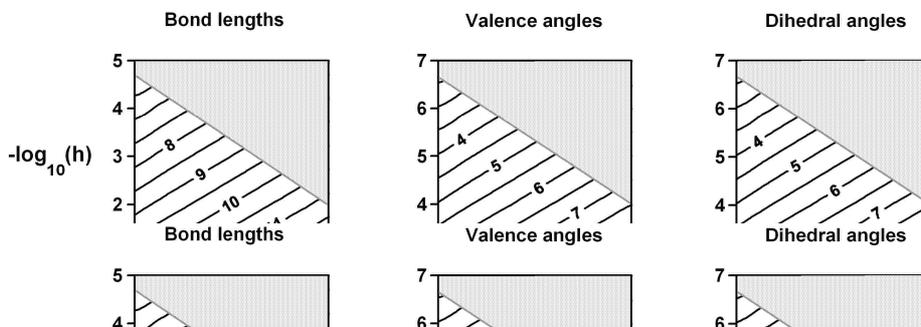
Fig. 4. Minus decimal logarithm of the numerical derivatives error in Glycolaldehyde. Equivalent results are obtained for Methyl formate and Ethyl methyl ether. The dotted zone represents forbidden combinations of step size and number of Richardson extrapolations.

n=9. In those cases, the error is found about 10^{-12} and 10^{-8} in distances and angles, respectively.

With the previous error data, an estimation of the number of significant digits can be obtained. To such an end we need to know the order of the derivatives. Thus, we compute average values for the distances and angles derivatives in Glycolaldehyde, Methyl formate and Ethyl methyl ether. The set of coordinates shown in Table 1 is used. Considering the three molecules, we obtain average values in the order of 10^{-2} for distances and between 1 and 10^{-1} for angles. These data, together with the previous estimations of the error, permit to obtain the number of significant digits in the procedure. Thus, using the proposed h and n combinations we have ten and eigth-seven significant digits for distances and angles, respectively.

4.4   Example: Vibrational G Matrix Information

As an example of application we compute the kinetic terms of the vibrational Hamiltonian corresponding to the torsional motions represented in Figure 3 for Glycolaldehyde,

Table 2. Vibrational kinetic constants for torsional motions in Glycolaldehyde, Methyl formate and Ethyl methyl ether molecules. The data are in cm^{-1}.

Kinetic Constant	Glycolaldehyde	Methyl Formate	t-Ethyl methyl ether
$B_{\theta 1}$	3.3998	3.3609	17.3545
$B_{\theta 2}$	21.2813	5.8001	7.1801
$B_{\theta 3}$	—	—	13.4695
$B_{\theta 1,\theta 2}$	-2.0337	-1.3724	-9.0109
$B_{\theta 1,\theta 3}$	—	—	-10.4427
$B_{\theta 2,\theta 3}$	—	—	6.8756

Methyl formate and Ethyl methyl ether. Using the optimal h and n combinations, the rovibrational G matrix is computed. Table 2 collects the vibrational kinetic terms obtained. Here, we have used the nomenclature $B_{ij} = \hbar^2 g_{ij}/2$. We observe that the kinetic coupling between the torsional motions (terms $B_{\theta 1, \theta 2}$, $B_{\theta 1, \theta 3}$ and $B_{\theta 2, \theta 3}$) has a significant weight. In particular, the coupling terms are especially important in Ethyl methyl ether. Therefore, these vibrational motions are strongly coupled. So, uncoupled vibrational models (even anharmonic) can not describe properly the torsional vibrational structure of these molecules. An anharmonic vibrational Hamiltonian, including the coupling among the coordinates, is needed.

5 Conclusions

In this work, we develop a methodology for the accurate numerical computation of the rovibrational G matrix. A C++ program is designed and presented for applying the methodology to the molecular structures obtained from any of the available electronic structure programs. To such an end we make use of polymorphism, one of the object orientation characteristics. The needed numerical derivatives are obtained from a Tailored Richardson extrapolation, using central differences for the starting estimation of derivatives. To optimize the procedure, we developed an error model of derivatives taking into account truncation and roundoff errors. Using a set of three floppy molecules we determine the optimal combination of step size and Richardson extrapolations, for computing the derivatives needed to obtain the G matrix in internal (curvilinear) coordinates. The data show uniform results for all the bond distances, on one side, and for all the valence and dihedral angles, on the other. Using the program, we compute the vibrational kinetic terms for several simultaneous torsional motions in Glycolaldehyde, Methyl formate and Ethyl methyl ether.

Acknowledgements

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