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Parameterizing a Simple Potential Energy Function Appropriate for Vibrational Frequencies Using Molecular Dynamics (and Maple, Java, Fortran versions of CDNT)

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A Maple scheme for quickly parameterizing vibrational potential energy functions is presented. As an example, the potential energy function's parameters for the vibrational motions in H_2O_2 are obtained assuming the simplest potential energy function.

This paper was originally written as a research paper, but rejected by the referees. It is therefore being edited into an "educational" paper for student usage.

I. INTRODUCTION I

When one learns about infrared spectroscopy and the internal vibrations of nuclei against each other inside a molecule (or solid) one starts with the diatomic molecule and the simple harmonic oscillator, and then, perhaps, graduates to triatomics, dealing with H_2O and/or CO_2 . Few among us proceeds further, since the mathematics as presented, is daunting. Here, we deal with the first non-trivial case, 4-atom molecules, using H_2O_2 as the prototype.

We attempt to guide the novice into several aspects of molecular dynamics of polyatomic molecule aggregates (we will treat single molecules here, but the idea should be clear how to extend the dynamics to more than one molecule). We start with the idea of how one generates the coordinates of the nuclei which are to be used as the starting point of any simulation. Specifically, we need the Cartesian coordinates of each nucleus, meaning a list of triples (x_i, y_i, z_i) while i runs over each nucleus, labelled arbitrarily.

Once we have the coordinates, we need to know the forces operating between the nuclei, usually based on inter-nuclear distances, but sometimes depending on torsional angles, or bond angles. No matter what, the potential energy function has to be translated into the same coordinate system as the molecule has used, usually Cartesian, so that one can conduct molecular mechanics integration of Newton's equations of motion for each nucleus subject to the forces induced by the potential energy scheme (generator of the forces).

We learn how to construct a molecule mathematically, using a fortran program (CDNT), a java equivalent program (JMakeMol), and finally a Maple program (CDNT). The three are all equivalent, doing their work in the same way, just using different modalities.

Finally, we deal with a Maple program which carries out the molecular dynamics on the CDNT-created molecule, leading to the vibrational frequencies (classical) which correspond in some measure to the quantum mechanical frequencies we are simulating.

So there are two parts to this paper. First, we create starting coordinates, and then second, we use Newton's second law ($F = ma$) to watch the dynamics of the nuclei subject to an internal potential energy function.

II. INTRODUCTION II

There is interest in efficiently assaying whether or not a given molecular force field generates vibrational frequencies acceptably close to those experimentally observed. A Maple [1] program is introduced which allows simple, direct, and efficient testing of molecular force fields and their parameters. Since the tool employed (Maple) "knows" calculus, no special coding of the partial derivatives of the potential energy with respect to the Cartesian coordinates of the various atoms is necessary, and therefore, the procedure is remarkably easy to apply to any reasonably sized molecule (clearly, very large molecules choke the computer, which is operating symbolically using very long strings as constructs rather than simple numbers).

Since hydrogen peroxide is one of the simplest molecules which displays little or no symmetry (S_2) and therefore does not succumb to symmetry simplifications, it is an apt test case for studying methods of rapidly parameterizing potential energy models.

Reported here are the parameters for a simple potential energy function applicable to this molecule which gives rise to atomic vibrations whose frequencies are reasonably close to experimental values derived from infra-red spectra of this molecule.

This paper indicates how, for larger molecules whose potential energy functions are not so well characterized, a "brute force" method of parameterizing a simple potential energy function can be carried out.

III. THE POTENTIAL ENERGY FUNCTION

A. Geometric Specification of the H_2O_2 Molecule

The scheme for naming this 4-atom molecule (H_2O_2) is to label the atoms in two ways, H_1 and H_2 are atoms 1 and 4, while atoms O_1 and O_2 are numbered atoms 2

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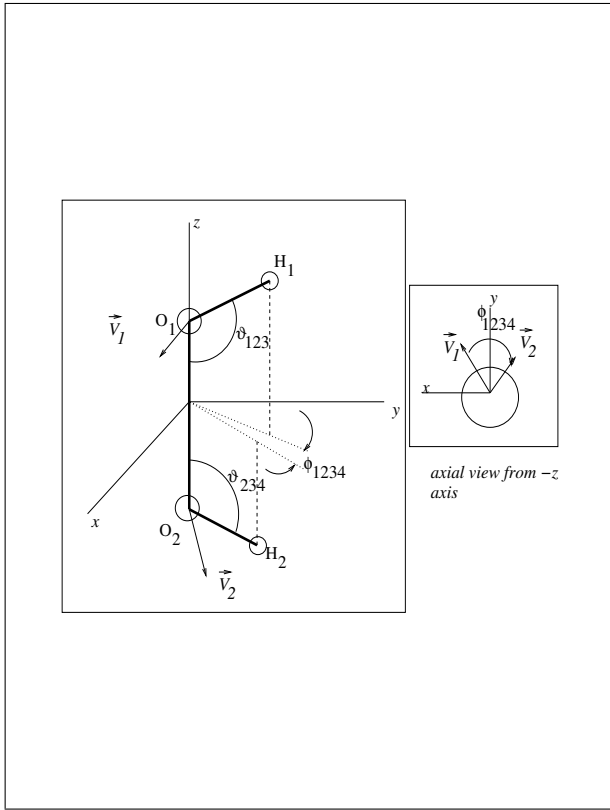


FIG. 1: Defining the angles in H_2O_2

and 3. Thus the bending angles are ϑ_{123} and ϑ_{234} , while the torsional angle is ϕ_{1234} . This is detailed in Figure 1.

The torsional angle needs special consideration. Defining the vectors $\vec{r}_{O_1-H_1}$ and $\vec{r}_{O_1-O_2}$ we have

$$\vec{V}_1 \equiv \vec{r}_{O_1-O_2} \times \vec{r}_{O_1-H_1}$$

and defining the vectors $\vec{r}_{O_2-H_2}$ and $\vec{r}_{O_2-O_1}$ ($= -\vec{r}_{O_1-O_2}$), we have

$$\vec{V}_2 \equiv \vec{r}_{O_2-O_1} \times \vec{r}_{O_2-H_2}$$

then, clearly [2],

$$\cos \phi_{1234} = \frac{\vec{V}_1 \cdot \vec{V}_2}{|\vec{V}_1||\vec{V}_2|}$$

We employ the Koput [3] and Reddington et al [4] approximate gas-phase structures, i.e., with the O-H equilibrium bond lengths set at 0.965\AA , the O-O equilibrium bond lengths set at 1.464\AA , the H-O-O equilibrium bond angles ($\vartheta_{OOH}^{eq} (= \vartheta_{123} = \vartheta_{234})$) set at 99.6° , for the H-O-O-H equilibrium twist angle ($\phi_{HOOH}^{eq} (\phi_{1234}) = 111.8^\circ$). [3].

B. A Candidate Potential Energy Function and its Parameters

A simple potential energy function [2]: which can be employed for this molecule's internal vibrations is:

$$V = \frac{k_{OH}}{2}(r_{12} - r_{OH}^{eq})^2 + \frac{k_{OH}}{2}(r_{34} - r_{OH}^{eq})^2 + \frac{k_{HOO}}{2}(\vartheta_{123} - \vartheta_{OOH}^{eq})^2 + \frac{k_{HOO}}{2}(\vartheta_{234} - \vartheta_{OOH}^{eq})^2 + \frac{V_0}{2}(\cos(\phi_{1234}) - \cos(\phi_{HOOH}^{eq}))^2 \quad (1)$$

The force constants taken from Praprotnik and Janežič [2] are shown in Table III. These values were used as the starting point in searching for the optimal set of values which replicate the infra red data reasonably well.

IV. MOLECULAR DYNAMICS OF A SINGLE MOLECULE

A Maple program has been constructed which contains the above noted potential energy function, along with analytical schemes for obtaining the partial derivatives of this potential energy function with respect to each of the 12 Cartesian coordinates which locate its 4 atoms. These partial derivatives are proportional to the force components acting on each of these nuclei. Using these expressions for the forces and the Verlet [5] algorithm, we integrate the Newtonian equations of motion for these nuclei, starting from positions which approximately mimic each (in turn) of the normal modes, searching for frequencies of vibration of these normal modes.

Starting with an "acceptable" equilibrium structure for hydrogen peroxide (see Table I), we can increase or decrease bond angles and/or lengths to approximately mimic a desired normal mode. Choosing such a normal mode means creating initial coordinates for the Maple program which accepts these coordinates as data. To create these coordinates, we've created a Java program which is a translation of the CDNT program discussed earlier [6].

For a chosen normal mode and a fixed parameterization of the potential energy function, we fine tune the vibrational simulation by choosing a time step (typically of the order of 10^{-16} seconds) trying to obtain an integral number of harmonic vibrations over the course of the simulation, which allows us to compute the frequency of vibration in a straightforward manner. This process can be repeated with different parameterizations of the potential energy function until agreement with the experimental vibrational frequency, ω_0 , for that particular normal mode, is achieved. Our results are shown in Table II along with other sets of data [7, 8]. Table III shows the potential energy parameters obtained in this work compared to earlier values. It should be noted that the values of Griguère and Bain[8] are for a more complicated potential energy model.

Isotopic substitution resulted in reasonable changes in the Maple generated vibrational frequencies as expected.

V. CONCLUSIONS

The simple potential energy function employed here, can be augmented in any manner which is analytically tractable, for use in the Maple program without coding anything other than the function itself. This makes testing different potential energy functions extremely simple to do.

It should be noted that molecules with rings or other complicated constraints are not included in the class of molecules that this program can address without more analysis and specialized programming. However, adjusting the code for 5, 6 or more atom molecules is straightforward.

It should further be noted that there are only four parameters in the H_2O_2 molecule's potential energy function used here, while there are six frequencies of vibration reported. Thus, the last two modes listed are "predicted" from these calculations, based on the parameters used in fitting the first four modes.

Finally, one notes that the H-O-O-H torsion vibration in the classical simulation is not necessarily equivalent to the tunneling quantum mechanical "motion" observed in the real molecule, nor should the reported frequency, which corresponds to an oscillation inside one well of a double-welled potential energy function, agree *a priori* with the reported infra-red transition observed.

The Maple code is available [9] for the H_2O_2 case and included as an Appendix here. In the same library one can find the java versions of the CDNT program (executable jar file, which also contains documentation, source code, input files, etc.).

VI. JAVA DOCUMENTATION

A. Introduction

JmakeMol is a Java program written under NetBeans 5.0 $\beta 2$. As this documentation is being written, there are several problems with Jmol and cdk, so what you see here is a hack which works, i.e., does the job, but is far from perfect. But "**Tempus fugit**", so as of March 2006, here's where we are.

There are two parts to JmakeMol which need to be addressed. The first is the computation of Cartesian coordinates when the input is bond angles and bond lengths for molecules. In an earlier life, I programmed a FORMAC version of a program known as CDNT[?], but, perhaps you know, FORMAC is dead, and the code for this program was lost a long time ago. I therefore resolved to re-program CDNT into Java for this project. Thanks to Prof. A. Rossi[?] a copy of the FORTRAN

code was obtained and converted to Java. This forms the core of JmakeMol. In separate postings in this repository can be found CDNT in both Java and Fortran.

B. CDNT (input)

Input to the program is very FORTRAN-like, i.e., a set of control cards. In this case, we use a free-format scheme where the delimiter between fields is the semi-colon, with each "card" image ending in a CR (carriage return).

The first "card" contains the number of bonds (2 digits, 04 as example), the number of atoms (2 digits, 05 as example), and the name (H as example, or H1) of the first atom. This atom is placed at the origin.

The second "card" and following ones, one for each bond, contains the starting atom number:ending atom number:bond length:bond angle (i-j-k): and the twist angle (i-j-k-l):atom name, all separated by colons. The "cards" are free-form, i.e., no need to line up things in columns.

Enclosed in the jar file is the hydrogen peroxide input data:

```
0304H
1:2:0.965 :    0.0 :    0.0:O
2:3: 1.464 :   99.6 :    0.0:O
3:4: 0.965 :   99.6 :  111.8:H
```

Note that the 1-2-3-4 twist angle is set at 111.8 degrees. That is an H-O-O-H dihedral angle, corresponding to the known structure.

C. CDNT (usage)

The program opens with an input file request. I suggest "*.inp" as the file type.

Once the program is running, two windows appear. One is a Jmol version of the molecule's pdb file as saved to the same directory in which the program found the inp file. The other is a rendition of the input file with a submit button. Editing the data in this window and re-submitting creates a new .inp_x file where x is an integer, and a new pdb file which is then rendered as a Jmol drawing.

The .inp file requires that each bond be located relative to two initial bonds, i1, and i2, which are placed, via hard-coding, at default locations with pseudo atoms at their termini.

To add a bond, we define its parent atom, its target atom, the bond length, the ζ value relative to the parent's

Parameter	Sumpter et al [10]	Praprotnik and Janežič	Koput(expt) [3]
r_{OH}	0.965 Å	0.988 Å	0.965 Å
r_{OO}	1.464 Å	1.453 Å	1.464 Å
ϑ_{OOH}	99.4°	102.7°	99.6°
ϕ_{HOOH}	111.5°	119.8°	111.8°

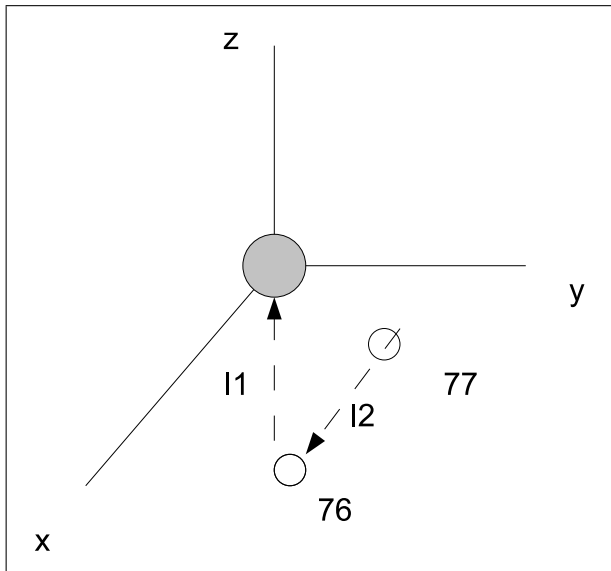
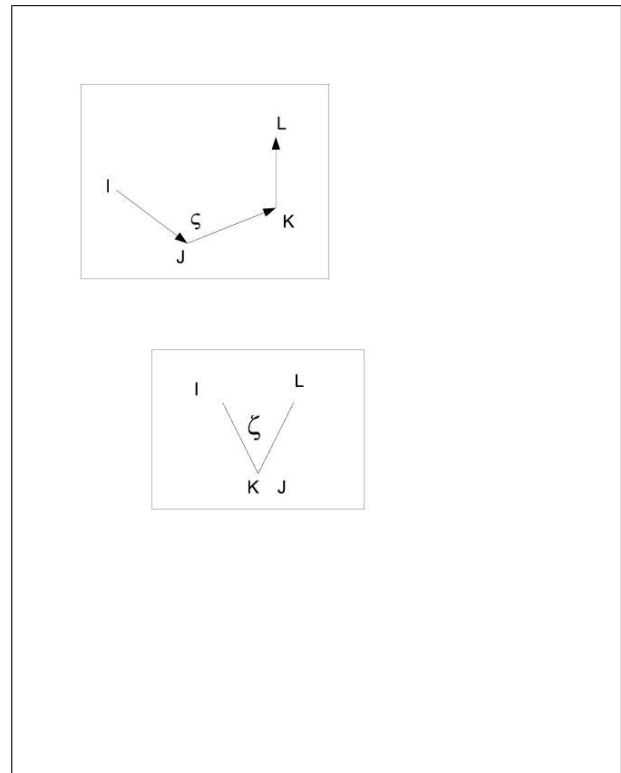
TABLE I: Geometric Parameters for H₂O₂ geometry

FIG. 2: Anchoring atoms 76 and 77 and the molecule's first atom shown at origin

parent, the parent, and the target atoms (ζ), and the η value relative to the past three atoms (relative to this last one).

FIG. 3: Atoms I, J and K define ζ , while atoms I, J, K and L define η .

mode number	description	Praprotnik and Janežič [2]	this work ^a	Harding[7]	Gigurère and Bain [8]
1	sym O-H stretch	3360	3620	3616	3610
2	sym bend	1421	1390	1392	1315
3	O-O stretch	878	852	859	877
4	H-O-O-H torsion	635	685		660
5	asym O-H stretch	3360	3580	3613	3614
6	asym O-O-H bend	1360	1400	1271	1266

^a3 sig. fig.

TABLE II: Normal Modes and Frequencies for H₂O₂ in cm⁻¹

Term	Praprotnik and Janežič [2]	Griguère and Bain [8]	this work
k_{OH}	$900 \frac{\text{kcal}}{\text{mole}\text{Å}^2} (6.25 \times 10^5 \text{ dynes/cm})$	$7.28 \times 10^5 \text{ dynes/cm}$	$1020 \frac{\text{kcal}}{\text{mole}\text{Å}^2} (7.09 \times 10^5 \frac{\text{dynes}}{\text{cm}})$
k_{OO}	$580 \frac{\text{kcal}}{\text{mole}\text{Å}^2} (4.02 \times 10^5 \text{ dynes/cm})$	$3.84 \times 10^5 \text{ dynes/cm}$	$500 \frac{\text{kcal}}{\text{mole}\text{Å}^2} (3.47 \times 10^5 \frac{\text{dynes}}{\text{cm}})$
k_{OOH}	$140 \frac{\text{kcal}}{\text{mol}\text{-rad}^2}$	0.89 mdyne Å	$137 \frac{\text{kcal}}{\text{mol}\text{-rad}^2} (0.951 \times 10^5 \frac{\text{dynes}}{\text{cm}})$
k_{HOOH}	$140 \frac{\text{kcal}}{\text{mol}\text{-rad}^2}$		$20 \frac{\text{kcal}}{\text{mol}\text{-rad}^2}$

TABLE III: Potential Energy Parameters for H₂O₂

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- [1] Any symbolic calculus program will do, Maple happens to be my choice here.
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 □ C. W. DAVID, *Constrained Variation of Molecular Geometry Using FORMAC*, Computers and Chemistry, 2, 65 (1978).
 □ A. Rossi, private communication, rossi@york.cuny.edu
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