

Geometry from Chemistry I

The Dynamics of Bucky Balls

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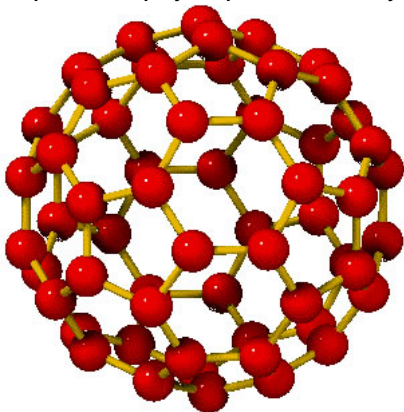
Rose-Hulman Institute of Technology
Rose Math Seminar

Outline

- 1 Introduction
 - bucky balls
- 2 Classical Dynamics
 - overview
 - tri-atomic molecules
 - dynamic equations
- 3 Harmonic behaviour
 - eigenvectors
 - simulations
- 4 Bucky Ball Geometry
 - labelling and geometry of local terms
- 5 Future Work

bucky ball - ball and stick model

- Here is a ball and stick model of a bucky ball from the site <http://www.psyclops.com/bucky.shtml>



- there are 60 atoms and 90 bonds

soccer ball

- a bucky ball looks like a soccer ball



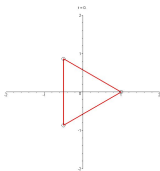
- the bonds of the bucky ball are the seams of the soccer ball
- the atoms are where the seams meet
- the bucky ball and the soccer ball have icosahedral symmetry
- this is important later

mechanics of a bucky ball vibrations

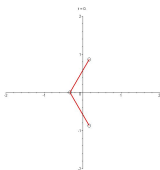
- use classical mechanics to describe the molecular vibrations of the bucky ball
- quantum models are needed to describe spectroscopic behaviour
- quantum models are beyond the scope of this talk
- bucky balls are large enough so that classical mechanics is useful
- we will develop the classical (Newtonian) mechanical model for triatomic models - easier and we have Maple demos

tri-atomic molecules

- consider tri-atomic models of two types (Maple pictures)



- an unrealistic triangle molecule



- a water molecule

setting up the dynamics 1

- describe a molecule in cartesian coordinates

$$\vec{X} = (X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3)$$

where atom i of mass m_i is given by $A_i = (X_i, Y_i, Z_i)$.

- a bucky ball has 180 variables and hence is complicated
- write

$$\vec{A}_i = (U_i, V_i, W_i) + (x_i, y_i, z_i)$$

(U_i, V_i, W_i) is the equilibrium position and (x_i, y_i, z_i) is the displacement

setting up the dynamics 2

- total energy = kinetic energy + potential energy
- kinetic energy is $T(\vec{X}) = \frac{1}{2} \sum_i m_i \frac{d\vec{A}_i}{dt} \bullet \frac{d\vec{A}_i}{dt}$
- potential energy is $V(\vec{X})$ for some function V
- thus $T(\vec{X}) + V(\vec{X}) = \text{constant}$
- T and V on depend only on the displacement from equilibrium

setting up the dynamics 3

- differentiate $T(\vec{X}) + V(\vec{X}) = \text{constant}$
- we get a system of second order D.E.'s which in vector form is

$$M \frac{d^2 \vec{X}}{dt^2} = - \nabla V(\vec{X})$$

where $\nabla = \text{gradient}$ and M is a mass matrix

- explain on board with one particle

setting up the dynamics 4

- there are two main problems
 - find $V(\vec{X})$
 - solve and interpret the dynamics equations
- methods
 - pose a model for $V(\vec{X})$ with a small number of parameters
 - ask a chemist what the parameters are - lots of work, use spectroscopy
 - use numerical simulation - could be tough

the harmonic limit

- write a Taylor series expansion at equilibrium

$$\nabla V(\vec{X}) = \vec{F}(\vec{X}) = \vec{F}_1(\vec{X}) + \vec{F}_2(\vec{X}) + \dots$$

- where $\vec{F}_i(\vec{X})$ is a vector function of the displacements and
- the components of $\vec{F}_i(\vec{X})$ are polynomials in the displacements of degree i
- for small vibrations we can ignore the higher order terms (linearize) and we get the harmonic limit equation

$$M \frac{d^2 \vec{X}}{dt^2} = \vec{F}_1(\vec{X})$$

or

$$\frac{d^2 \vec{X}}{dt^2} = M^{-1} \vec{F}_1(\vec{X})$$

eigenvectors 1

- we assume that everything has mass 1 (change of coordinates)
- there is a matrix H (Hessian matrix of second partials of V at equilibrium) such that

$$\frac{d^2\vec{X}}{dt^2} = -H\vec{X}$$

- H is a symmetric matrix with positive eigenvalues (except for motion and rotation directions)
- and a linearly independent set of eigenvectors.

eigenvectors 2

- suppose \vec{E} is a unit eigenvector for eigenvalue $\lambda > 0$
- consider a solution of the form $\vec{X}(t) = u(t)\vec{E}$
- from the dynamics equation

$$\frac{d^2}{dt^2} (u(t)\vec{E}) = -Hu(t)\vec{E} = -\lambda u(t)\vec{E}$$

or

$$\frac{d^2}{dt^2} u(t) = -\lambda u(t)$$

or

$$u(t) = A \cos(\sqrt{\lambda}t + \phi)$$

eigenvectors 3

- every solution has the form

$$\sum_i A_i \cos(\sqrt{\lambda_i} t + \phi_i) \vec{E}_i$$

- this is the normal mode decomposition
- $A_i \cos(\sqrt{\lambda_i} t + \phi_i) \vec{E}_i$ is a normal mode



simulations

- now we look at some Maple simulations and some board work
- threebody-threebonds.mws
- body3-bond2angle1.mws

local terms 1

- terms of the potential for small vibrations generally only depend on a few atoms
- 2-body terms - bonds - as in `threebody-threebonds.mws`
- 3-body terms - angles - as in `body3-bond2angle1.mws`
- 4-body terms - puckering terms - tetrahedral volumes

local terms 2

- 2-body terms - bonds
- let $R_{i,j} = \|\vec{A}_i - \vec{A}_j\|$ and $R_{i,j}^0$ be the equilibrium value
- then $k_{i,j} \left(R_{i,j} - R_{i,j}^0 \right)^2$ is a possible term near equilibrium

local terms 3

- 3-body terms - angles
- let $\{i, j, k\}$ be indices so that the atom i is bonded to both atoms j and k
- let $\Theta_{i,j,k}$ be the angle determined by the triple, based at atom i , and $\Theta_{i,j,k}^0$ be the equilibrium value
- then $k_{i,j,k} \left(\Theta_{i,j,k} - \Theta_{i,j,k}^0 \right)^2$ is a possible three body term near equilibrium

local terms 4

- 3-body terms - dot products
- since $(\vec{A}_j - \vec{A}_i) \bullet (\vec{A}_k - \vec{A}_i) = R_{i,j} R_{i,k} \cos(\Theta_{i,j,k})$ we might try the following
- set $D_{i,j,k} = (\vec{A}_j - \vec{A}_i) \bullet (\vec{A}_k - \vec{A}_i)$, $D_{i,j,k}^0$ the equilibrium value
- then $k_{i,j,k} (D_{i,j,k} - D_{i,j,k}^0)^2$ is a possible three body term near equilibrium

local terms 5

- 4-body terms - puckering terms - tetrahedral volumes
- let $\{i, j, k, l\}$ be four atoms forming a tetrahedron on the bucky ball with atoms j, k, l connected to atom i , refer to the bucky ball slide
- let $T_{i,j,k,l}$ be the volume of the tetrahedron and $T_{i,j,k,l}^0$ the equilibrium value
- then $k_{i,j,k} \left(T_{i,j,k,l} - T_{i,j,k,l}^0 \right)^2$ is a possible four body term near equilibrium
- computing the partial derivatives of the tetrahedral volume is an interesting multi-variable calculus exercise

local terms 6

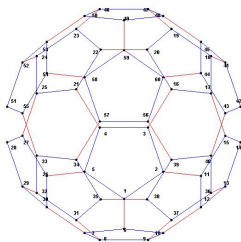
- How does the geometry of the Bucky Ball fit in?
- write the potential as a sum over 2-body, 3 body and 4 body terms

$$V(\vec{X}) = \sum_{i,j} V(\vec{A}_i, \vec{A}_j) + \sum_{i,j,k} V(\vec{A}_i, \vec{A}_j, \vec{A}_k) + \sum_{i,j,k,l} V(\vec{A}_i, \vec{A}_j, \vec{A}_k, \vec{A}_l)$$

- a sum over 2-body, 3 body and 4 body terms
- little interaction from atoms far apart
- use bucky geometry to label coordinates and keep track of nearby neighbours - see next slide

labelling 1

- bucky ball labels using the symmetry group



future work

- exact computation of gradients
- rapid calculation of gradients
- adding anharmonic terms - transfer of energy between modes
- stronger use of group theory in adding anharmonic analysis