

# Geometry from Chemistry I

## The Dynamics of Bucky Balls

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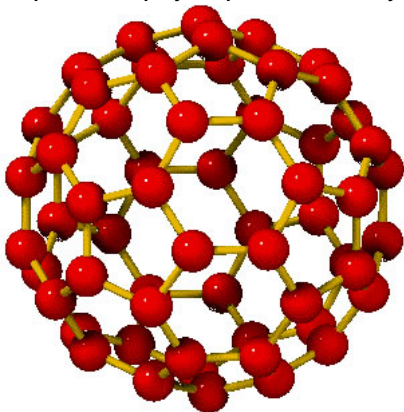
Rose-Hulman Institute of Technology  
Rose Math Seminar

# 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



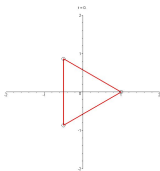
- the bonds of the bucky ball are the seams of the soccer ball
- the atoms are where the seams meet
- the bucky ball and the soccer ball have icosahedral symmetry
- this is important later

# mechanics of a bucky ball vibrations

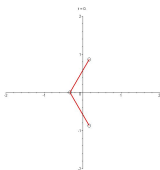
- use classical mechanics to describe the molecular vibrations of the bucky ball
- quantum models are needed to describe spectroscopic behaviour
- quantum models are beyond the scope of this talk
- bucky balls are large enough so that classical mechanics is useful
- we will develop the classical (Newtonian) 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 with  $N$  atoms in cartesian coordinates

$$\vec{X} = (X_1, Y_1, Z_1, X_2, Y_2, Z_2, \dots, X_N, Y_N, Z_N)$$

with atom  $i$  of mass  $m_i$  given by  $\vec{A}_i = (X_i, Y_i, Z_i)$ .

- 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 of  $H$  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

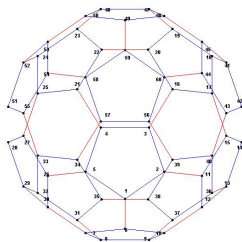
- How does the geometry of the Bucky Ball fit in?
- write the potential as a sum over 2-body, 3 body and 4 body terms

$$V(\vec{X}) = \sum_{i,j} V_2(\vec{A}_i, \vec{A}_j) + \sum_{i,j,k} V_3(\vec{A}_i, \vec{A}_j, \vec{A}_k) + \sum_{i,j,k,l} V_4(\vec{A}_i, \vec{A}_j, \vec{A}_k, \vec{A}_l)$$

- 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