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Geometry from Chemistry II - The Geometry of Nanotubes

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Geometry from Chemistry II

The Geometry of Nanotubes

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assists by authors of our forthcoming book
SCIENCE OF NANOTECHNOLOGY: An introductory text

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Rose Math Seminar
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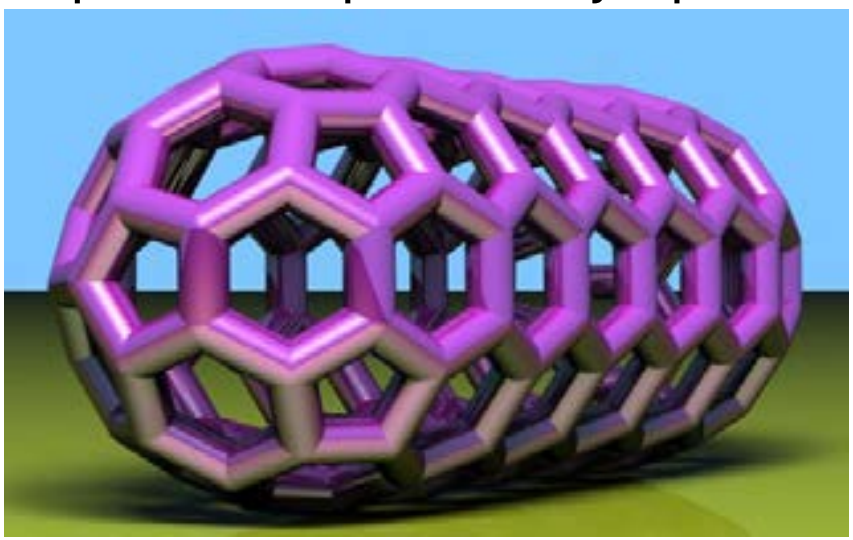
Outline

1. Introduction
   - nanotubes
2. Basic Structure
   - number of pentagons
   - graphene sheets
   - nanotubes from graphene sheets
3. Symmetries
   - cylindrical coordinates and nanotube map
   - symmetries
4. Labelling and Potential Energy
   - local potential energy terms
5. Future Work

nanotube - cartoon picture - 1

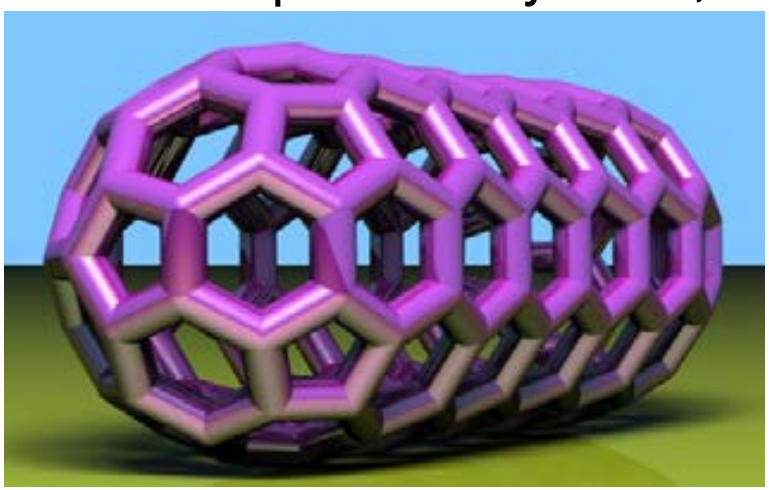
- Here is a cartoon model of a small single walled carbon nanotube (SWT) from the site http://www.icpf.cas.cz/jiri/pictures/nanotube.jpg

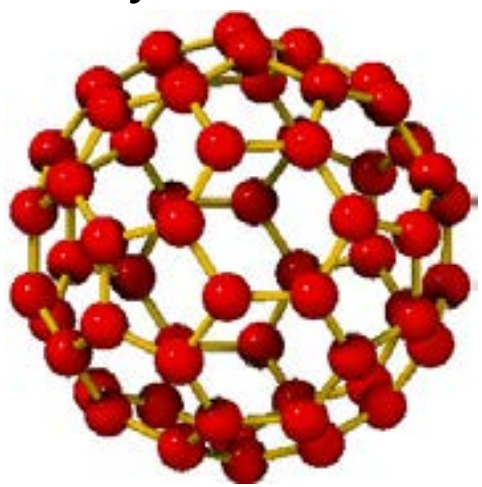


- other pictures later

nanotube - cartoon picture - 2

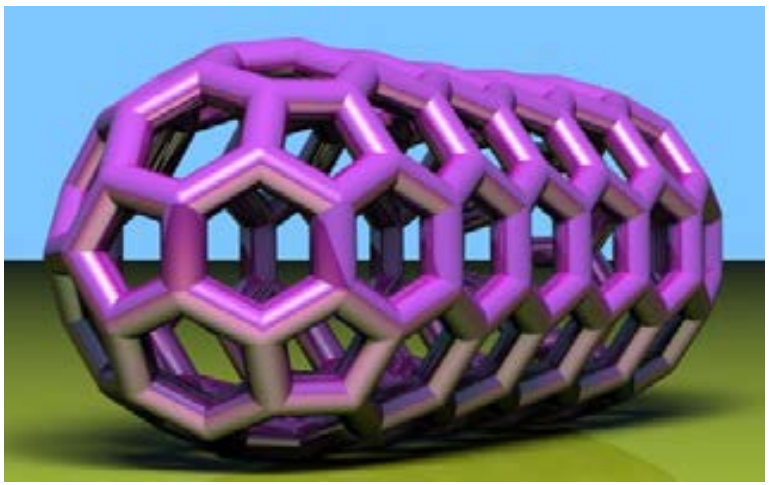
- SWT's are very interesting chemical objects and hold great promise for utilization in the future. The already have many uses today.
- we are going to focus on the geometry of SWT's
- from the pictures you can see that can be thought of as more complex bucky balls, in fact they are fullerenes.





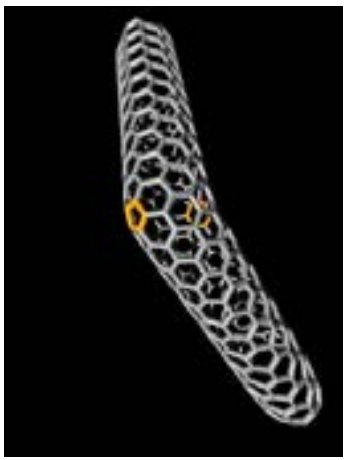
number of pentagons - 1

- bucky balls and nanotubes are examples of trivalent graphs on a sphere (squeeze/stretch a nanotube so that it looks like a sphere)
- look at nanotube and soccer ball model of a bucky ball



- trivalency because of the chemical bonding model (sp^2 bonding)

number of pentagons - 2

- because of stability reasons, regions defined on the sphere are usually pentagons or hexagons
- sometimes there are heptagons though heptagons (or unusually placed pentagons) may cause a kink
- 

number of pentagons - 3

- there are twelve pentagons on the bucky ball (look at the soccer ball again) 

- There are always twelve pentagons on any nanotube!

number of pentagons - 4

- Proof: Let $h = \#hexagons$, $p = \#pentagons$.
- graph is on a sphere so
- 2 = euler characteristic = $\#faces - \#edges + \#vertices$

$$2 = p + h - \frac{5p + 6h}{2} + \frac{5p + 6h}{3}$$

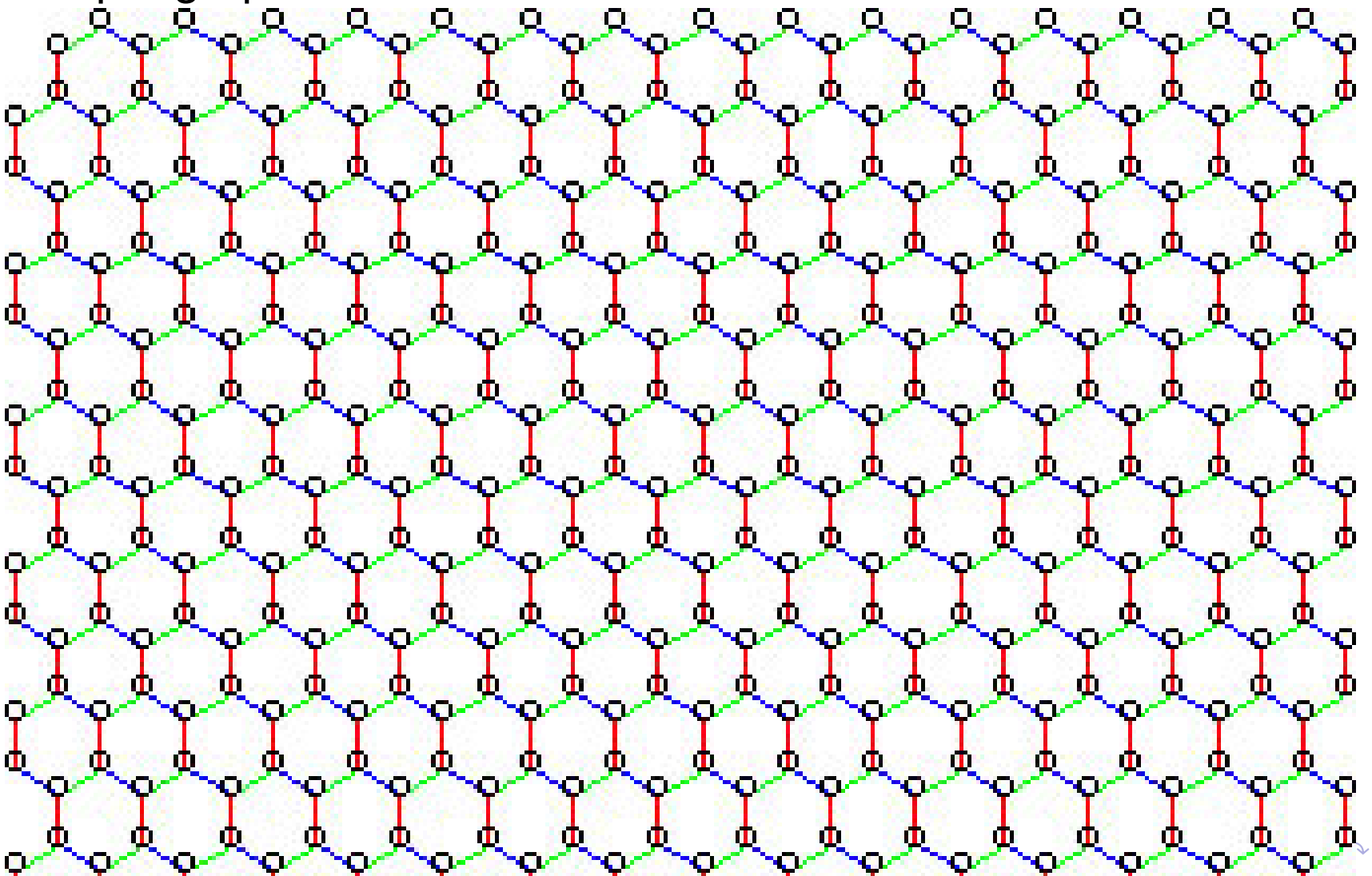
- simplify to get $2 = p/6$ or $p = 12$

graphene sheet - 1

- a graphene sheet is a planar hexagonal arrangement of atoms - see next page or handout
- nanotubes are “rolled up" graphene sheets, more about this ahead
- several of the sheets weakly bonded together in parallel form graphite
- in the real world we do not get a finite region but we will assume the graphene sheet is infinite to simplify the mathematics
- observe that every atom located lies at the top or bottom of a unique hexagon, where blue and green edges meet.
- call these “up” atoms and “ down” atoms.

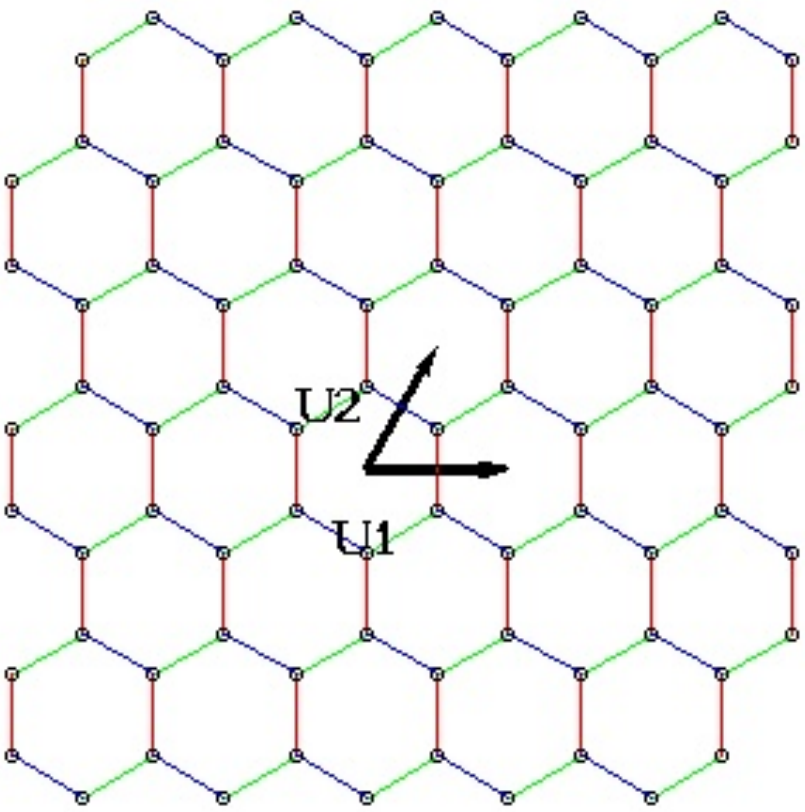
graphene sheet - 2

- sample graphene sheet



graphene sheet coordinates - 1

- consider the two vectors $\mathbf{U}_1$ and $\mathbf{U}_2$



graphene sheet coordinates - 2

- where

$$\mathbf{U}_1 = a(1,0)$$

$$\mathbf{U}_2 = a\,(\cos 60^\circ, \sin 60^\circ) = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$$

  and a is the bond length to make things simple we are going to assume that $a = 1$
- every point in the plane $P = (x, y)$ can be uniquely written as a linear combination of the two vectors $\mathbf{U}_1$ and $\mathbf{U}_2$ i.e.,

$$P = u\mathbf{U}_1 + v\mathbf{U}_2$$

- u and v are integers if and only if P is the center of a hexagon

nanotube from graphene sheet - 1

- loosely roll up the graphene sheet into a “nanotube”, choose any direction to roll then adjust the sheet until the patterns match up on the overlap
- puncture the sheet on the overlap at the center of two hexagons
- unroll the sheet and draw a lines between the pairs of punctures.
- you should get parallel vectors, you always get a parallel vector no matter what hexagon is punctured

nanotube from graphene sheet - 2

- in the infinite plane two hexagons determine the same hexagon on the nanotube if their centers differ by a multiple of the roll-up vector
- express the resulting “chiral” or “roll-up” vector **C** in the form

$$\mathbf{C} = n\mathbf{U}_1 + m\mathbf{U}_2$$

- m and n determine the nanotube up to rotation.
- also by rotation one may assume that the m and n satisfy $0 \leq m \leq n$
- we call the nanotube (n, m) - nanotube

nanotube - cartoon picture - 2

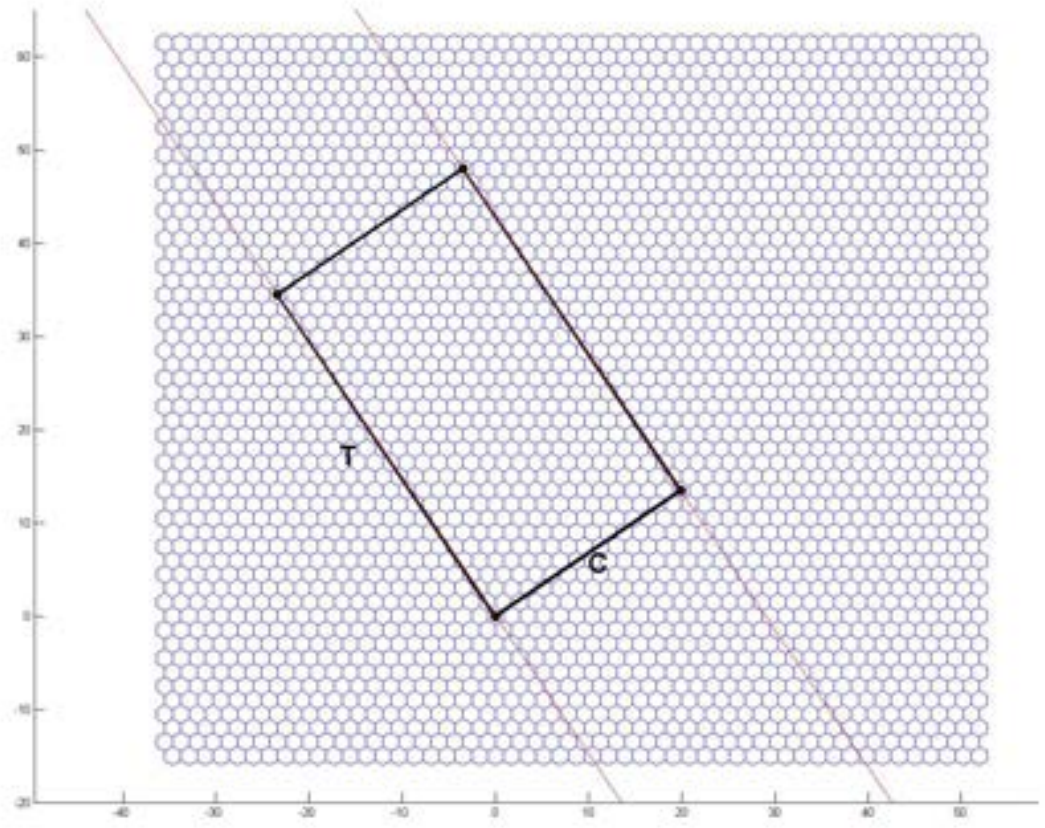
- cartoon pictures of nanotube sections with $(n, m) = (7, 7)$ and $(n, m) = (5, 9)$

nanotube region and unit cell - 1

- draw two lines perpendicular to **C** and passing through the ends of a vector - picture next slide
- every hexagon on the nanotube comes from exactly hexagon in between the lines (need to make some kind of choice if center is on a line).
- nanotube can be constructed by cutting along the lines and pasting.

nanotube region and unit cell - 2

- nanotube region and unit cell for a $(9, 7)$-nanotube



nanotube region and unit cell - 3

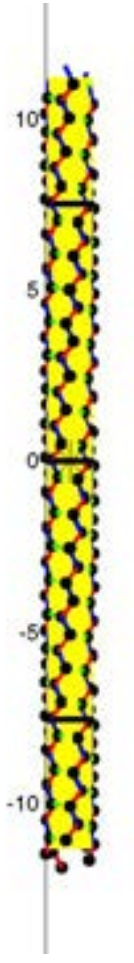
- find the first hexagon on the region of the boundary whose center lies on the nanotube boundary passing through the base of **C**, refer to last slide
- call the vector so determined by **T** and write

$$\mathbf{T} = t_1\mathbf{U}_1 + t_2\mathbf{U}_2$$

  for appropriate integers
- the rectangle determined by **C** and **T** when rolled up is like the surface of a tin can
- This finite cylinder is called a unit cell, the nanotube is formed by stacking together many copies of the unit cell.

nanotube region and unit cell - 4

- two unit cells on a skinny nanotube



nanotube region and unit cell - 5

- easy to show that

$$t_1 = -(n + 2m)/d$$

and

$$t_2 = (2n + m)/d$$

where

$$d = \gcd(n + 2m, 2n + m)$$

cylindrical coordinates and nanotube map - 1

- consider cylindrical coordinates (θ, z) along the nanotube (nanotube axis is the vertical z-axis)
- map from plane coordinates to $\mathbf{X} = (x, y)$ to cylindrical coordinates is given by

$$z = z(\mathbf{X}) = \frac{\mathbf{X} \bullet \mathbf{T}}{\|\mathbf{T}\|}$$

$$\theta = \theta(\mathbf{X}) = 2\pi \frac{\mathbf{X} \bullet \mathbf{C}}{\|\mathbf{C}\|^2}$$

- the map to 3D coordinates is

$$\phi : \mathbf{X} \to \frac{\|\mathbf{C}\|}{2\pi} \left(\cos(\theta)\vec{i} + \sin(\theta)\vec{j} \right) + z\vec{k}$$

cylindrical coordinates and nanotube map - 2

- observe that

$$z(\mathbf{X} + \mathbf{C}) = z(\mathbf{X})$$

$$\theta(\mathbf{X} + \mathbf{C}) = \theta(\mathbf{X}) + 2\pi$$

  so that

$$\phi(\mathbf{X} + \mathbf{C}) = \phi(\mathbf{X})$$

- equivalent hexagons on the graphene sheet map to the same hexagon on the nanotube
- the nanotube cartoon on the slide second next was produced using this map

symmetries - 1

- symmetry: transformation of the nanotube that takes hexagons to hexagons
- almost all are twists: translations

$$z \longrightarrow z + z_0$$

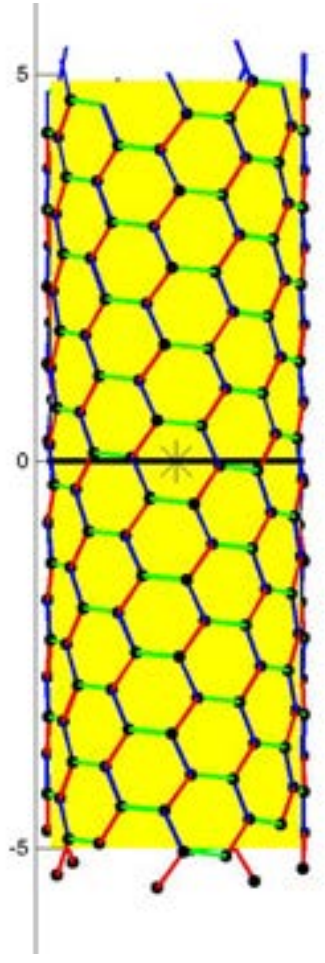
followed by a rotation

$$\theta \longrightarrow \theta + \theta_0$$

- some of these are obvious by following along the twists (see next slide)
- there must be some relationship between z_0 and θ_0
- Fact: for every pair of hexagons there is a symmetry taking one hexagon to the other (because this is true on the graphene sheet)

symmetries - 2

- there are three obvious twist- symmetries on this tube



local terms - 1

- from Lecture I we saw that the potential energy was important to dynamics of molecules
- little interaction from atoms far apart so a the potential energy is a sum of local terms
- terms of the potential for small vibrations generally only depend on a few atoms
- 2-body terms - bonds
- 3-body terms - angles
- 4-body terms - puckering terms - tetrahedral volumes

local terms - 2

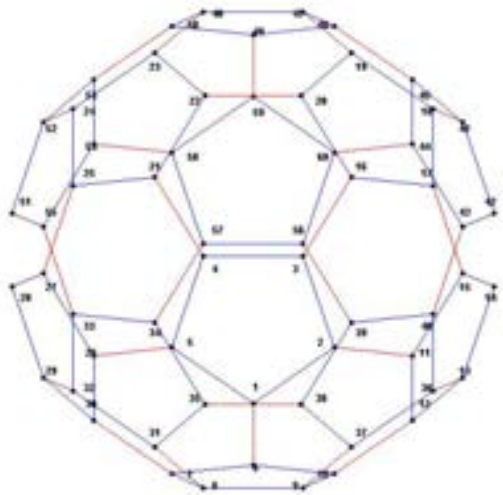
- How does the geometry of the bucky ball or the nanotube fit in?
- write the potential as a sum over 2-body, 3-body and 4-body terms ($\vec{A}_i$ is the i'th atom)

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

- in potential and gradient calculations use bucky or nanotube geometry geometry to label coordinates and keep track of nearby neighbours (first and second)
- see next slide for bucky ball

labelling - 1

- bucky ball labels using the symmetry group



labelling - 2

- Fact: if $\gcd(n, m) = 1$ the hexagons of a nanotube can be labelled by the integers in such a way that neigbouring hexagons are obtained by adding small fixed integers to the current index
- the process is simple using only 2D linear algebra and the Euclidean algorithm for finding the greatest common divisor m and n
- Matlab movie of indexing nanopics.m

labelling - 3

- Method: use the Euclidean algorithm to find integers q and p so that $nq - mp = 1$, i.e.,

$$\det\left(\begin{bmatrix} q & p \\ n & m \end{bmatrix}\right) = 1$$

and set

$$\mathbf{K} = q\mathbf{U}_1 + p\mathbf{U}_2$$

- the labelling map is

$$s \to \phi(s\mathbf{K})$$

labelling - 4

- Why it works: first

$$\begin{bmatrix} \mathbf{K} \\ \mathbf{C} \end{bmatrix} = \begin{bmatrix} q & p \\ n & m \end{bmatrix} \begin{bmatrix} \mathbf{U}_1 \\ \mathbf{U}_2 \end{bmatrix}$$

so that

$$\begin{bmatrix} \mathbf{U}_1 \\ \mathbf{U}_2 \end{bmatrix} = \begin{bmatrix} m & -p \\ -n & q \end{bmatrix} \begin{bmatrix} \mathbf{K} \\ \mathbf{C} \end{bmatrix}$$

- Suppose that $\vec{A}$ is the "up" atom of hexagon with center $\mathbf{L} = s\mathbf{K} + t\mathbf{C}$
- the nearest neighbours are the down atoms of the hexagons with centers $\mathbf{L} + \mathbf{U}_2$, $\mathbf{L} - \mathbf{U_1} + \mathbf{U}_2$ and $\mathbf{L} - \mathbf{U_1} + \mathbf{2U}_2$

labelling - 5

- Since $\mathbf{U}_1 = m\mathbf{K} - p\mathbf{C}$ and $\mathbf{U}_2 = -n\mathbf{K} + q\mathbf{C}$ then

$$\mathbf{L} + \mathbf{U}_2 = s\mathbf{K} + t\mathbf{C} - n\mathbf{K} + q\mathbf{C} = (s - n)\mathbf{K} + (t + q)\mathbf{C}$$

$$\mathbf{L} - \mathbf{U}_1 + \mathbf{U}_2 = (s - m - n)\mathbf{K} + (t + p + q)\mathbf{C}$$

$$\mathbf{L} - \mathbf{U}_1 + 2\mathbf{U}_2 = (s - m - 2n)\mathbf{K} + (t + p + 2q)\mathbf{C}$$

- the labels of the hexagons are then going to be $s - n$, $s - m - n$, and $s - m - 2n$

future work for bucky balls and nanotubes

- exact computation of gradients
- rapid calculation of gradients
- Do any of the dynamics of the bucky ball apply well to nanotubes?
- what are the dominant normal modes of bucky balls.
- adding anharmonic terms - transfer of energy between modes
- stronger use of group theory in the anharmonic analysis