

## Learning Molecular Geometry and Symmetry through hands-on Mathcad Exercise.©

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### Goal

This work sheet will help you work on symmetry operations of molecules from conceptual graph operations to algebraic manipulations that you can do with Mathcad. Reducing 3-dimensional graphical operations into algebra is an advantage as it will help you analyze the problem better and learn about group theory applications to chemistry. Examples in these worksheets are water molecule ( $C_{2v}$  symmetry group), ammonia ( $C_{3v}$ ), methane ( $T_d$  symmetry group), and benzene ( $D_{6h}$  symmetry group)

### Prerequisites

1. Experience with matrix algebra and geometry operations on molecular symmetry. The skills include ability to calculate a transpose, inverse, and determinant of a matrix, and ability to determine eigenvectors and eigenvalues.
2. Moderate manipulative skills with Mathcad.
3. Some basic programming skills with Mathcad.

### Performance Objectives

At the end of this exercise you will be able to:

1. define bond vectors from molecular coordinate data;
2. define symmetry operations with matrix operators;
3. demonstrate group theory principles using matrix algebra;
4. discover unitary properties for these symmetry operations.
5. discover Hermitian properties for quantum operators.

### Mathcad matrix operation tutorial.

If this is the first time you have been exposed to Mathcad matrix operations, or if you are just a novice on this subject, you are encouraged to try out: **Introduction to Matrices--A Tutorial for Physical Chemists**, written by **Dr. Melissa S. Reeves** of Turkegee University. The Mathcad matrix toolbars are very useful for you to insert matrices and find the inverse, transpose, determinants, dot products, and vector products of matrices.

**Warm-up Exercise 1:** Create a space in this work sheet, insert an arbitrary 3x3 matrix, find the inverse, transpose, and determinants using the matrix toolbars. Check the Mathcad results with your hand calculations (or the results from your hand calculators) to convince yourself that your initial efforts are successful.

**Warm-up exercise 2: Symmetric and Hermitian Matrix.** Create a symmetric 3x3 matrix and verify that its transpose is equal to itself. Which of the following 3x3 matrices are Hermitian matrices ?

$$a1 := \begin{pmatrix} 2 & 2 + 3i & 6 - 2i \\ 2 + 3i & 6 & 4 - 3i \\ 6 - 2i & 4 - 3i & 7 \end{pmatrix} \quad a2 := \begin{pmatrix} 2 & 2 + 3i & 6 - 2i \\ 2 - 3i & 6 & 4 - 3i \\ 6 + 2i & 4 + 3i & 7 \end{pmatrix} \quad a3 := \begin{pmatrix} 2 & 2 + 3i & 6 - 2i \\ 3 + 2i & 6 & 4 - 3i \\ 2 - 6i & 3 - 4i & 7 \end{pmatrix}$$

Hint: A symmetric matrix is defined as a matrix such that its transpose is the same as the original matrix itself, or

$$A^T := A$$

A Hermitian matrix is defined as such that the transpose conjugate of a matrix is the same as the original matrix itself, or

$$\overline{(A^T)} := A$$

Mathcad matrix toolbars do not have a conjugate button. To get a conjugate of a matrix, you type " next to your matrix.

Mathcad uses either **i** or **j** to produce a complex number. Type a number in front of **i** or **j** without a multiplying sign. Example:

$$a := 1 + 3j \quad \bar{a} = 1 - 3i$$

$$\text{or} \quad a := 1 + 3i \quad \bar{a} = 1 - 3i$$

**Warm-up exercise 3: Eigenvalue and eigenvectors** If you do not know what eigen vectors or eigen values are, you are encouraged to refer to any Linear Algebra textbook. Here is an example of such a textbook: **Mathematical Methods for Scientists and Engineers, by Donald McQuarrie, University Science Books, 2003.** Find eigenvectors and eigenvalues for **a1, a2, and a3 in Warm-Up Exercise 2.** An example for finding eigenvalues and eigenvectors for **a1** is illustrated here.

$$\text{eigenvecs}(a1) = \begin{pmatrix} 0.448 + 0.086i & -0.592 + 0.321i & -0.553 - 0.141i \\ 0.475 + 0.04i & 0.718 & -0.464 + 0.272i \\ 0.752 & -0.064 - 0.162i & 0.621 \end{pmatrix}$$

$$\text{eigenvals}(a1) = \begin{pmatrix} 13.493 - 2.191i \\ 1.974 - 2.22i \\ -0.467 + 4.41i \end{pmatrix}$$

Notice that the eigenvalues for a non-Hermitian matrix are not necessarily real.

**Warm-up exercise 4: Properties of Hermitian and Symmetric Matrices** Convince yourself that the eigenvectors corresponding to distinct eigenvalues of a symmetric matrix (Warm-up Exercise 2) are orthogonal while the eigenvalues for Hermitian matrices (a2 in Warm-up Exercise 2) are real numbers.

**Subscripts, and vectors.** Mathcad uses [ for matrix subscript. To retrieve a matrix element  $a$  from the row  $i$  and column  $j$ , you type  $a[ij$ . (On the other hand, Mathcad uses . for a subscript for a given variable name. This could be confusing in the beginning. But you will get used to it.)  $a[00$  is the element  $a$  from first row and first column. What is  $a[3,2$ ?

**Example:**

$$X := \begin{pmatrix} 2 & 4 & 8 \\ 5 & 8 & 7 \\ 3 & -2 & -6 \end{pmatrix} \quad X_{2,2} = -6 \quad \text{The element on the third row and third column of X is -6.}$$

The vector is retrieved using a superscript <>. The first column vector is superscript <0>, second column vector is superscript <1>, etc.

**Warm-up exercise 5:** Create an arbitrary 3 x 3 matrix, and retrieve a vector from the second column of the matrix. Also retrieve an element from the second row and third column.

Example: Go back to a1 in Warm-up Exercise 2;

$$a1 = \begin{pmatrix} 2 & 2 + 3i & 6 - 2i \\ 2 + 3i & 6 & 4 - 3i \\ 6 - 2i & 4 - 3i & 7 \end{pmatrix} \quad a1^{(0)} = \begin{pmatrix} 2 \\ 2 + 3i \\ 6 - 2i \end{pmatrix}$$

You can do the rest for  $a1^{<1>}$ , and  $a1^{<2>}$ .

**Scatter Plots in Mathcad** Creating a scatter plot in Mathcad is easy. Insert-Graph-3D scatter plot sequence will lead you to plot 3D scatter. Mathcad will plot an array of vectors  $X$  shown above, or  $(X, Y, Z)$  three vectors representing  $x, y, z$ , coordinates.

**Warm-up exercise 6:** Create a scatter plot ( $X^{<0>}$ ,  $X^{<1>}$ , and  $X^{<2>}$ ), for an arbitrary 3x3 matrix,  $X$ . How many points do you see in this scatter plot? What are the  $(X,Y,Z)$  coordinates of these 3 points in the plot? How are these coordinates related to the original matrix,  $X$ ?

Example:

$$X := \begin{pmatrix} 3 & 2 & 1 \\ 7 & 0 & 4 \\ 5 & -2 & 9 \end{pmatrix} \quad X^{<0>} = \begin{pmatrix} 3 \\ 7 \\ 5 \end{pmatrix} \quad X^{<1>} = \begin{pmatrix} 2 \\ 0 \\ -2 \end{pmatrix} \quad X^{<2>} = \begin{pmatrix} 1 \\ 4 \\ 9 \end{pmatrix}$$

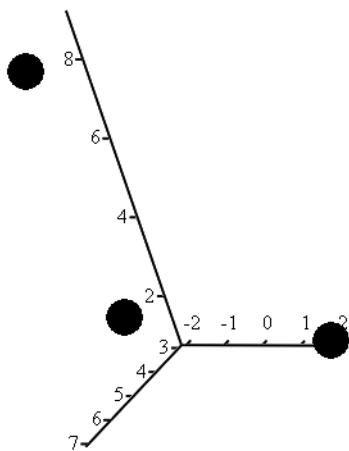


Fig. 1 A graphic representation of a molecule by atomic coordinates.

$$(X^{<0>}, X^{<1>}, X^{<2>})$$

There are 3 points in the scatter plot. What are the coordinates of these 3 points?

**Plotting Vectors in Scatter Plots** If I want to plot vectors connecting the origin to those 3 points in Warm-up Exercise 6, I would insert origin coordinate to vectors,  $X^{<0>}$ ,  $X^{<1>}$ , and  $X^{<2>}$ . In the scatter plot, I would use "connecting lines" in the "line option" of "Format" dialog box.

**Warm-up exercise 7:** With the matrix,  $X$ , from Warm-up Exercise 6, plot vectors originated from  $(0,0,0)$  to these 3 points.

Example: We repeat three vectors:  $X^{<0>}$ ,  $X^{<1>}$ , and  $X^{<2>}$

$$X^{<0>} = \begin{pmatrix} 3 \\ 7 \\ 5 \end{pmatrix} \quad X^{<1>} = \begin{pmatrix} 2 \\ 0 \\ -2 \end{pmatrix} \quad X^{<2>} = \begin{pmatrix} 1 \\ 4 \\ 9 \end{pmatrix}$$

Add origin to these 3 vectors.

$$X1^{(0)} := \begin{pmatrix} 0 \\ 3 \\ 0 \\ 7 \\ 0 \\ 5 \end{pmatrix} \quad X1^{(1)} := \begin{pmatrix} 0 \\ 2 \\ 0 \\ 0 \\ 0 \\ -2 \end{pmatrix} \quad X1^{(2)} := \begin{pmatrix} 0 \\ 1 \\ 0 \\ 4 \\ 0 \\ 9 \end{pmatrix}$$

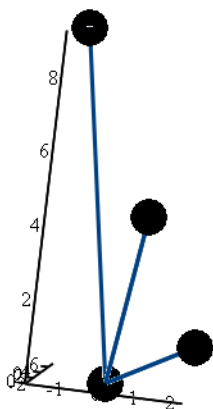


Fig.2 Graphic representation of a molecule by vectors.

$$(X1^{(0)}, X1^{(1)}, X1^{(2)})$$

You will find that plotting vectors originating from origin is very useful in the following discussions of symmetry operations of molecules.

## Symmetry operations

All symmetry operations in 3-dimensional space can be represented by 3x3 matrices. The simplest, E operation, is represented by a 3x3 identity matrix created by the command identity(3). A rotation of angle  $\theta$  along z-axis is represented by: In the space to the right type identity(3)= to see the 3x3 identity matrix..

$$\text{Rot}(z, \theta) := \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad [\text{Eq.1}] \text{ See McQuarrie and Simon's Physical Chemistry, A Molecular Approach, 1997, page 441}$$

In general, a rotation of angle  $\theta$  about any unit vector, A, passing through the origin, is represented by:

$$\text{Rot}(A, \theta) := \cos(\theta) \cdot \text{identity}(3) + \sin(\theta) \cdot \begin{pmatrix} 0 & -A_2 & A_1 \\ A_2 & 0 & -A_0 \\ -A_1 & A_0 & 0 \end{pmatrix} + (1 - \cos(\theta)) \cdot A \cdot A^T \quad \text{Eq.[2]}$$

See Glassner, A., **Graphic Gems I**, Associated Press, 1990. Also see: Martin John Baker's Website: <http://www.euclideanspace.com/maths/geometry/rotations/index.htm>

It is to be understood that all symmetry matrices in this work will operate on a displacement vector (x,y,z)

To check if Eq [2] reduces to Eq[1], let's define

$$A := \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \text{Eq. [2a]; A is a unit vector in the z-direction.}$$

$$\text{Rot}\left(A, \frac{\pi}{2}\right) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is the matrix representing a rotation of 90 degree about the z-axis. We will then use Eq.[2] throughout the discussions.

A reflection by a plane that is perpendicular to the z-axis is represented by  $\sigma$ :

$$\sigma := \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{Eq.[3]}$$

In general, a reflection by a plane passing through the origin, that is perpendicular to a unit vector,  $A$ , is represented by a  $\text{Refl}(A)$  matrix:

$$\text{Refl}(A) := \text{identity}(3) - 2 \cdot A \cdot A^T$$

Let us check this equation to see if the matrix reduces to Eq.[3] when  $A$  is a unit vector along z-axis:

$$\text{Refl}(A) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

An inversion about the origin is represented by an  $\text{Inv}$  matrix:

$$\text{Inv} := -\text{identity}(3) \quad \text{Eq. [4]}$$

These few matrices will give us sufficient tools to conduct algebraic operations on molecules.

**Exercise 1:** Write an arbitrary unit vector and write a 90 degree rotation matrix, a reflection matrix on a plane that is perpendicular to this unit vector. Find the determinants of these two matrices. What do you discover? These symmetry matrices are often called unitary matrices. Do you know why?

## Water molecule

The coordinates of the water molecule can be obtained from quantum computations using software such as HyperChem. In HyperChem, you need to align the molecule such that z-axis is the axis of the rotation. In setting up the molecule for quantum computation, you need to use "Align Viewer" with the z-axis (This assures you are looking down the z-axis.) Next, align the tertiary axis (axis of rotation in water) with the z-axis, using "Align Molecules" and align the tertiary axis with the z-axis.

After the alignment, perform ab-initio calculations with 6-31G\*\*, Restricted Hartree-Fock with MP correlation. Go to the log to find your coordinate data. The unit of length used in this matrix is the Angstrom.

$$\begin{array}{c}
 \mathbf{x} \quad \mathbf{y} \quad \mathbf{z} \\
 i := 0..2 \\
 \text{H2O} := \begin{pmatrix} 0.25466 & -2.56367 & 0 \\ -0.16998 & -1.72171 & 0 \\ 1.181036 & -2.38703 & 0 \end{pmatrix} \begin{array}{c} \mathbf{O} \\ \mathbf{H} \\ \mathbf{H} \end{array}
 \end{array} \quad \text{Eq [5]}$$

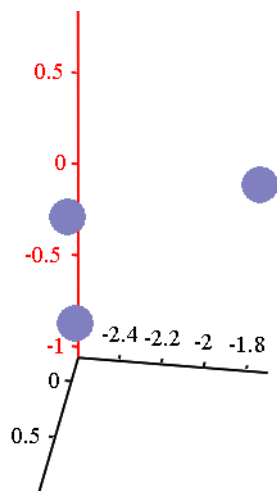
First column represents the x-coordinate of three atoms; 2nd column, the y-coordinates; 3rd column, the z-coordinates. First row represents (x,y,z) for the oxygen atom; two hydrogen atoms are represented by the second-row and third-row of the matrix.

If we want to graphically represent 2 OH bonds in the water molecule, we may want to express water molecule matrix as follows:

$$\begin{array}{c}
 \mathbf{x} \quad \mathbf{y} \quad \mathbf{z} \\
 \text{H2Ob} := \begin{pmatrix} 0.25466 & -2.56367 & 0 \\ -0.16998 & -1.72171 & 0 \\ 0.25466 & -2.56367 & 0 \\ 1.181036 & -2.38703 & 0 \end{pmatrix} \begin{array}{c} \mathbf{O} \\ \mathbf{H1} \\ \mathbf{O} \\ \mathbf{H2} \end{array}
 \end{array} \quad \text{Eq. 5a}$$

**Graphical representation of water molecule:**

$$\text{water}_i := \text{H2O}^{\langle i \rangle} \qquad \text{waterb}_i := \text{H2Ob}^{\langle i \rangle}$$



$j := 0..1$

Rotate the cube as you wish on this work sheet. You can observe that three atoms are in the same plane with  $z=0$ .

Fig 3: Graphic representation of a water molecule by atomic coordinates.

water

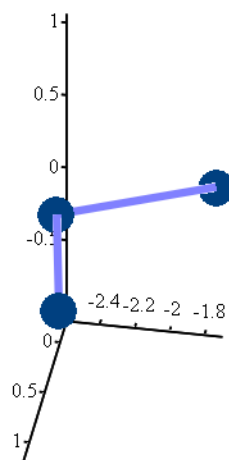


Fig 4. Graphic representation of a water molecule by 2 OH bonds.

waterb

## Internal Coordinates

Fig 4 can be further simplified, if we use internal coordinates such that the oxygen atom is set as the origin, and the principal axis of rotation is set as the z-axis.

By subtracting (x,y,z) coordinates of O from H1(and H2), we have r1 and r2 as coordinates of two hydrogen atoms.

$$\text{NewH}_2\text{O} := \begin{pmatrix} \text{x} & \text{y} & \text{z} \\ 0 & 0 & 0 \\ 0.926 & 0.177 & 0 \\ -0.425 & 0.842 & 0 \end{pmatrix} \begin{matrix} \text{O} \\ \text{H1 (r1)} \\ \text{H2 (r2)} \end{matrix} \quad [\text{Eq 5b}]$$

We still need to define the principal axis of rotation, which is a unit vector between 2 O-H bonds .

## C2 Rotation along a principal axis

Closely look at the water molecule shown in Fig.4, the principal axis of rotation is a unit vector between 2 O-H bonds. A 180 degree rotation along this unit vector, the molecule returns to itself. This axis of rotation is defined as the C2 rotation for the water molecule. To see this, we shall first define 2 r vectors, r1= r<0> and r2=r<1>, connecting O atom to 2 H atoms.

$$r^{(j)} := (\text{H}_2\text{O}^T)^{(j+1)} - (\text{H}_2\text{O}^T)^{(0)}$$

$$r = \begin{pmatrix} \text{OH1} & \text{OH2} \\ r^{(0)} & r^{(1)} \\ -0.425 & 0.926 \\ 0.842 & 0.177 \\ 0 & 0 \end{pmatrix} \begin{matrix} \text{x} \\ \text{y} \\ \text{z} \end{matrix} \quad \text{Eq [6]}$$

$$A := \begin{matrix} a \leftarrow \frac{r^{(0)} + r^{(1)}}{2} \\ \frac{a}{|a|} \end{matrix} \quad \text{A C2 rotation is Rot (A, } \pi) \quad \begin{matrix} |r^{(0)}| = 0.943 \\ |r^{(1)}| = 0.943 \end{matrix} \quad \text{Eq.[7]}$$

$$\text{Rot}(A, \pi) \cdot r = \begin{pmatrix} 0.926 & -0.425 \\ 0.177 & 0.842 \\ 0 & 0 \end{pmatrix}$$

We can see C2 on r1 returns as r2. You can try C2 on r2 to see if they return as r1.

Eq [8]

**Exercise 2:** Write  $x, y, z, r1, r2,$  and  $OH1 OH2$  above and beside the matrix in Eq [8] similar to those written on Eq.[6]

**Align C2 axis with a unit vector along the z axis** The procedures to align principal axis of rotation with a unit vector along the z-axis involve rotation operations through 3 consecutive Euler angles.

Unit vectors:  $x := \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$        $y := \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$        $z := \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

$$\text{cosine}(r1, r2) := \frac{r1^T \cdot r2}{|r1| \cdot |r2|} \quad \text{angle}(r1, r2) := \text{acos}(\text{cosine}(r1, r2)) \quad \text{Eq [9]}$$

$$\text{angle}(A, x)_0 = 63.776 \text{ deg}$$

$$\text{angle}(A, y)_0 = 26.224 \text{ deg}$$

$$\text{angle}(A, z)_0 = 90 \text{ deg}$$

From a treatise on rotations:

Pitch Transformation (rotate about current y axis):  $P(\theta) := \begin{pmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{pmatrix}$

Yaw Transformation (rotate about current z):  $Y(\theta) := \begin{pmatrix} \cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Roll Transformation (rotate about current x axis):  $R(\theta) := \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & \sin(\theta) \\ 0 & -\sin(\theta) & \cos(\theta) \end{pmatrix}$

Euler angle rotation is:

about the z-axis  
about the new y-axis  
about the new x-axis

$$\text{Euler}(\alpha, \psi, \phi) := R(\phi) \cdot P(\alpha) \cdot Y(\psi) \quad (\text{Eq.}[10])$$

in that order.

To align A with the z axis, we first rotate A about z-axis with an angle of  $\psi=(90-26.224)$  degree. This essentially align A with the x-axis. A second rotation of 90 degree will align A with z axis.

We can experiment the rotation operation as follows:

$$\psi := 90 \cdot \text{deg} - \text{angle}(A, y)_0 \quad \psi = 63.776 \text{ deg}$$

First rotation:

$$Y(\psi) \cdot A = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

This is a unit vector along x-axis.

Apply a second rotation:

$$P(90 \cdot \text{deg}) \cdot Y(\psi) \cdot A = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

This essentially is a unit vector along z-axis.

The succinct notation is shown as follows:

$$R1 := \text{Euler}(90 \text{deg}, \psi, 0 \text{deg}) \cdot A \quad R1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

The Euler operator defined in Eq.[10] can be used to linearly transform both OH bonds as follows:

$$\begin{aligned} \text{OH1} &:= \text{Euler}(90 \cdot \text{deg}, \psi, 0 \cdot \text{deg}) \cdot r^{\langle 0 \rangle} & \text{OH1} &= \begin{pmatrix} 0 \\ 0.753 \\ 0.568 \end{pmatrix} & |\text{OH1}| &= 0.943 \\ \text{OH2} &:= \text{Euler}(90 \cdot \text{deg}, \psi, 0 \cdot \text{deg}) \cdot r^{\langle 1 \rangle} & \text{OH2} &= \begin{pmatrix} 0 \\ -0.753 \\ 0.568 \end{pmatrix} & |\text{OH2}| &= 0.943 \end{aligned} \quad \text{Eq[11]}$$

### Plotting bond vectors

Define a new water molecule matrix:

$$\text{NewH2O} := \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.753 & 0.568 \\ 0 & 0 & 0 \\ 0 & -0.753 & 0.568 \end{pmatrix}$$

Eq [12]

$$\text{Rot}(R1, \pi) \cdot \text{OH1} = \begin{pmatrix} 0 \\ -0.753 \\ 0.568 \end{pmatrix}$$

$$\text{Rot}(R1, \pi) \cdot \text{OH2} = \begin{pmatrix} 0 \\ 0.753 \\ 0.568 \end{pmatrix}$$

C2 rotation on OH1 results in OH2. Similarly, C2 rotation on OH2 results in OH1.

$$i := 0..2 \quad \text{Nwater}_i := \text{NewH2O}^{(i)}$$

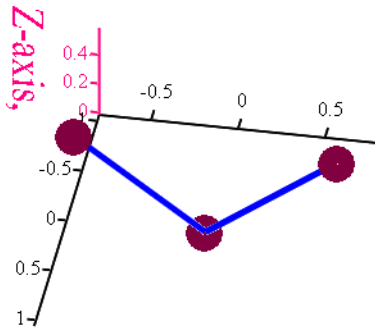


Fig. 5 Water molecule after aligning the C2 axis along the z-axis.

Nwater

**Exercise 3** Write  $x$ ,  $y$ ,  $z$ ,  $O$ ,  $H1$ ,  $H2$  over or beside the matrix  $\text{NewH2O}$  (Eq.[12]) similar to those shown in Eq [5b].

## Angle between the two O-H bonds

**Exercise 4:** If there are two vectors,  $a$  and  $b$ , that intersect with an angle  $\theta$ , how would you express the relationship between  $\theta$ , and the dot product of  $a$  and  $b$ ?

$$\text{angle} := \arccos\left(\frac{\mathbf{r}^{\langle 0 \rangle} \cdot \mathbf{r}^{\langle 1 \rangle}}{|\mathbf{r}^{\langle 0 \rangle}| \cdot |\mathbf{r}^{\langle 1 \rangle}|}\right) \quad \text{angle} = 105.968 \text{ deg} \quad \text{Eq [9]}$$

Calculate the angle between OH1 and OH2. Are they the same as the angle calculated from  $r^{\langle 0 \rangle}$  and  $r^{\langle 1 \rangle}$ ? Is this angle the same as the angle you had learned in your freshmen chemistry textbook? If not, what is the percentage of difference? Can you explain the difference?

## Reflection by a plane containing a principal axis

There are two such planes. One such plane is such that its normal is a vector that connects H1 to H2. The other plane is a plane containing all three atoms.

$$A1 := \begin{cases} \mathbf{a} \leftarrow \text{OH2} - \text{OH1} \\ \frac{\mathbf{a}}{|\mathbf{a}|} \end{cases} \quad \begin{array}{l} A1 \text{ unit vector is along H1-H2} \\ A2 \text{ unit vector is a unit vector along x-axis} \end{array} \quad A2 := \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\sigma_{v1} := \text{Refl}(A1) \quad \sigma_{v2} := \text{Refl}(A2)$$

$$\sigma_{v1} \cdot \text{OH1} = \begin{pmatrix} 0 \\ -0.753 \\ 0.568 \end{pmatrix} \quad \sigma_{v2} \cdot \text{OH1} = \begin{pmatrix} 0 \\ 0.753 \\ 0.568 \end{pmatrix} \quad \text{Eq [13]}$$

Reflection of OH1 vector with  $\sigma_{v1}$  returns OH2 and vice versa. Reflection of OH1 with  $\sigma_{v2}$  returns to itself.

## Symmetry operators for water molecule form a group

We can show that these 4 symmetry operators, E, C<sub>2</sub>, σ<sub>v1</sub>, and σ<sub>v2</sub> form a group, according to group theory. We need to demonstrate:

- 1) if A and B are symmetry operations of the group, then AB is also a symmetry operation of the group.
- 2) associative rule is obeyed: (AB)C= A(BC)
- 3) there is an identity symmetry operation, E, such that EA=AE=A
- 4) for every A, there is A<sup>-1</sup> such that AA<sup>-1</sup>=A<sup>-1</sup>A=E

With Fig.5 of OH1 and OH2 of water molecules, we re-write these 4 operators.

E := identity(3)

$$C_2 := \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{v1} := \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{v2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{Eq [14]}$$

**Exercise 5** Show these symmetry elements satisfy Group Property [1]: If A, and B are elements of a group then AB is an element of a group.

**Exercise 6** Demonstrate the associative property for these elements: If A, B, C are elements of a group, then (AB)C=A(BC)

**Exercise 7** What is the inverse of the element of C<sub>2</sub> ? Is the inverse of C<sub>2</sub> also a member of the group? What is it ?

## Unitary properties of symmetry operations

We can show these symmetry operations are unitary by showing that their transpose matrices are also their inverse matrices.

$$C_2^T = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_2^{-1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_2^T := C_2^{-1} \quad \text{Eq [15a]}$$

You may also notice that the determinants for these matrices are either +1 or -1:

$$|E| = 1 \quad |C_2| = 1 \quad |\sigma_{v1}| = -1 \quad |\sigma_{v2}| = -1 \quad \text{Eq [15b]}$$

**Exercise 8:** Are these symmetry matrices Hermitian (the transpose of a conjugate equals to itself) ? If they are, what are their eigenvalues?

**Exercise 9:** Are these symmetry matrices symmetric ( the transpose equals to itself) ?

**Exercise 10:** Are the eigenvectors of these matrices orthonormal ? An example of orthonormal properties for C2 is shown here.

$$e_{C2} := \text{eigenvecs}(C2) \quad e_{C2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{Eq [16]}$$

$$e_{C2}^{\langle 0 \rangle T} \cdot e_{C2}^{\langle 1 \rangle} = (0) \quad e_{C2}^{\langle 1 \rangle T} \cdot e_{C2}^{\langle 2 \rangle} = (0) \quad |e_{C2}^{\langle 0 \rangle}| = 1 \quad \text{Eq [17]}$$

The consequence of unitary operations implies that the lengths of these bond vectors are conserved. The proof of this theory can be found in McQuarrie's text, **Mathematical Methods for Scientists and Engineers**, page 460, 2003. Examples of these property is shown in the following exercises:

**Exercise 11** Demonstrate the unitary property of these symmetry matrices. An example of conservation of length is demonstrated here. You will need to demonstrate length conservations with other operators.

$$\text{Recall} \quad OH1 = \begin{pmatrix} 0 \\ 0.753 \\ 0.568 \end{pmatrix} \quad OH2 = \begin{pmatrix} 0 \\ -0.753 \\ 0.568 \end{pmatrix} \quad \text{Eq [18]}$$

$$|OH1| = 0.943 \quad |OH2| = 0.943$$

$$|(C2 \cdot r)^{\langle 0 \rangle}| = 0.943 \quad |(C2 \cdot r)^{\langle 1 \rangle}| = 0.943 \quad \text{Eq [19]}$$

**Exercise 12:** Recall that the unit generated from HyperChem for atomic coordinates is Angstrom. Is the bond length of 0.943 A or 94.3 pm reasonable ? Check your freshmen chemistry textbook to see how well these two values agree.



ammonia<sub>1</sub> := NNH3  $\langle i \rangle$

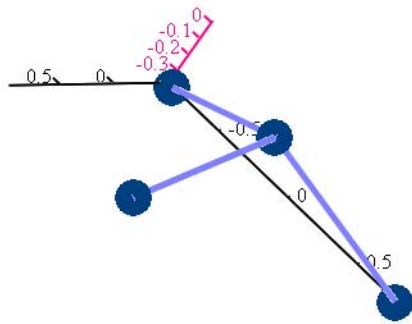


Fig 6 The ammonia molecule

ammonia

### Angles between N-H bonds

Define  $\text{angle}(a, b) := \text{acos}\left(\frac{a \cdot b}{|a| \cdot |b|}\right)$  Eq [22]

**Exercise 13:** Determine the angles between two arbitrary NH bonds. How close are these angles to the tetrahedral angles?

**Exercise 14:** What are the bond lengths for any of the NH bonds? Are the bond lengths reasonable?

### C3 Rotation

$$A := \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad C3 := \text{Rot}\left(A, \frac{2\pi}{3}\right)$$

$$C3 \cdot r = \begin{pmatrix} -0.466 & 0.932 & -0.466 \\ 0.808 & -2.642 \times 10^{-4} & -0.808 \\ -0.364 & -0.364 & -0.364 \end{pmatrix} \quad C3 \cdot r := \begin{pmatrix} -0.466 & 0.932 & -0.466 \\ 0.808 & 0 & -0.808 \\ -0.364 & -0.364 & -0.364 \end{pmatrix} \quad \text{Eq [23]}$$

The right-hand side matrix for C3\*r is essentially the same as the left-hand side matrix in Eq.[23] except the numerical value  $-2.642 \times 10^{-4}$  for  $C3 \cdot r_{11}$  on the left is set to zero on the right. The matrix is disabled by right-clicking on the box to disable the evaluation.

**Exercise 15** *Is C3 a Hermitian operator? Is C3 a symmetric operator? If not, find the eigenvalues and eigenvectors for C3. Are the eigenvalues real numbers? Are the eigenvectors orthonormal?*

### $\sigma$ Reflection

These reflection planes are perpendicular to vectors: H1-H2, H2-H3, and H3-H1

**Exercise 15:** *Write three vectors that are perpendicular to the reflection planes. One of the vectors is written here as A1. Write the other two vectors.*

$$A1 := \begin{pmatrix} a \leftarrow \text{NH}_3^{(2)} - \text{NH}_3^{(1)} \\ a \\ |a| \end{pmatrix} \quad \text{Eq [24]}$$

Recall

$$r = \begin{pmatrix} 0.932 & -0.466 & -0.466 \\ 0 & -0.807 & 0.807 \\ -0.364 & -0.364 & -0.364 \end{pmatrix}$$

**Exercise 16** Demonstrate that the ammonia molecule has three such reflection planes of symmetry. One demonstration is shown here. Complete the rest.

$$\text{Refl}(A1) \cdot r = \begin{pmatrix} -0.467 & 0.932 & -0.466 \\ -0.807 & -9.098 \times 10^{-5} & 0.808 \\ -0.364 & -0.364 & -0.364 \end{pmatrix} \quad \text{Refl}(A1) \cdot r := \begin{pmatrix} -0.467 & 0.932 & -0.466 \\ -0.807 & 0 & 0.808 \\ -0.364 & -0.364 & -0.364 \end{pmatrix}$$

$$\text{Recall} \quad r = \begin{pmatrix} 0.932 & -0.466 & -0.466 \\ 0 & -0.807 & 0.807 \\ -0.364 & -0.364 & -0.364 \end{pmatrix} \quad \text{Eq [25]}$$

**Exercise 18** Construct coordinate matrices based on Eq[25] and plot them to demonstrate that the molecule returns to an identical configuration after the reflection operations.

### Reflection-Rotation(Improper Rotation) of Methane Molecules

**Hyperchem Quantum Computation to collect coordinate data.** Your objective is to write 4 vectors from the central carbon atom to each individual H-atom. The goal of this hands-on exercise is to learn about the improper rotation,  $S_4$ , which is one of the symmetry operations for methane. You also need to show that there is no  $C_4$  symmetry operation for this particular molecule.

The units used in the following table are Angstroms.

	C	H1	H2	H3	H4	
CH4 :=	-0.59644	0.10993	-0.05909	-1.17164	-1.26497	x
	0.00448	0.09185	-0.02464	-0.90649	0.85720	
	0.58888	1.40590	-0.35160	0.70459	0.59666	)

Eq [26]

You need to write 4-CH vectors, and check whether they are tetrahedrally oriented. The experience you have gained through the previous ammonia exercises will help you to write such vectors.

$j := 0..3$

$$r^{(j)} := \text{CH4}^{(j+1)} - \text{CH4}^{(0)}$$

CH1	CH2	CH3	CH4	
0.706	0.537	-0.575	-0.669	)
0.087	-0.029	-0.911	0.853	
0.817	-0.94	0.116	$7.78 \times 10^{-3}$	)

Eq [27]

**Exercise 19** Find the bond angles between any of these 4 bonds. Find the bond lengths for all these bonds. Do they agree with the definition of a tetrahedral molecule?

### Plotting methane molecule

Construct a matrix

$$\text{CCH4} := \begin{pmatrix} 0 & 0 & 0 \\ -0.669 & 0.853 & 0 \\ 0 & 0 & 0 \\ -0.575 & -0.911 & 0.116 \\ 0 & 0 & 0 \\ 0.537 & -0.029 & -0.94 \\ 0 & 0 & 0 \\ 0.706 & 0.087 & 0.817 \end{pmatrix}$$

Eq.[28]

**Exercise 20** Write  $x, y, z, C, H1, H2, H3, H4$  over or beside the matrix CCH4 (Eq.[28]) similar to those shown in Eq [5b].

$$i := 0..2 \quad \text{methane}_i := \text{CCH4}^{(i)}$$

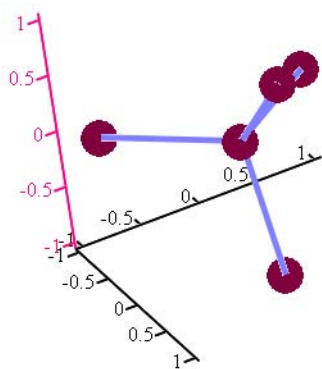


Fig 7 The methane molecule

methane

The methane molecule has an reflection-rotation symmetry, S<sub>4</sub>, which consists of a combination of first, a 90 degree of rotation followed by a reflection which is perpendicular to this axis of rotation. By looking at the plot shown above, is the axis of rotation the same as z-axis ? Obviously, it is not. Therefore, you need to identify the axis of rotation.

The axis of rotation is half way between any of two C-H bonds.

**Exercise 21:** Find all the axes of rotation-reflection for methane. One of the axes is shown here. Find the other axes. How many of these axes are unique?

$$A := \begin{pmatrix} a \leftarrow r^{(1)} + r^{(3)} \\ a \\ |a| \end{pmatrix}$$

This little program says that a new axis of rotation A, is a unit vector half way between C-H1 and C-H3 bonds.

Eq [29]

$$C4 := \text{Rot}\left(A, \frac{\pi}{2}\right)$$

Now, let us look at the C<sub>4</sub> operation about A with each CH bond of the CH<sub>4</sub> molecule. What do you discover?

Recall

$$r = \begin{pmatrix} 0.706 & 0.537 & -0.575 & -0.669 \\ 0.087 & -0.029 & -0.911 & 0.853 \\ 0.817 & -0.94 & 0.116 & 7.78 \times 10^{-3} \end{pmatrix} \quad C4 \cdot r^{(0)} = \begin{pmatrix} 0.669 \\ -0.853 \\ -7.777 \times 10^{-3} \end{pmatrix} \quad \text{Eq[30]}$$

You can see that none of the column vectors in r<sup><0></sup> is the same as C<sub>4</sub>\*r. On the other hand, as for the rotation-reflection operator, S<sub>4</sub>\*r=Refl(A)\*C<sub>4</sub>\*r

$$S4 := \text{Refl}(A) \cdot C4 \quad \text{Eq [31]}$$

$$r = \begin{pmatrix} 0.706 & 0.537 & -0.575 & -0.669 \\ 0.087 & -0.029 & -0.911 & 0.853 \\ 0.817 & -0.94 & 0.116 & 7.78 \times 10^{-3} \end{pmatrix} \quad S4 \cdot r^{(0)} = \begin{pmatrix} 0.537 \\ -0.029 \\ -0.94 \end{pmatrix}$$

After the S<sub>4</sub> operation, r<sup><0></sup> becomes r<sup><1></sup>. You can repeat the operation for other column vectors.

**Exercise 22** Using other axes of rotation, construct new S<sub>4</sub> matrices. Does S<sub>4</sub> on these new axes return the molecule to itself its original configuration?

### ***S4 in methane is not Hermitian, it is unitary***

Recall

$$S_4 = \begin{pmatrix} -0.011 & 0.814 & 0.58 \\ -0.676 & -0.433 & 0.596 \\ -0.736 & 0.386 & -0.556 \end{pmatrix} \quad \text{eigenvals}(S_4) = \begin{pmatrix} i \\ -i \\ -1 \end{pmatrix} \quad \text{Eq [32]}$$

Two out of three eigenvalues for  $S_4$  are imaginary. But  $S_4$  is unitary.

$$S_4^T = \begin{pmatrix} -0.011 & -0.676 & -0.736 \\ 0.814 & -0.433 & 0.386 \\ 0.58 & 0.596 & -0.556 \end{pmatrix} \quad S_4^{-1} = \begin{pmatrix} -0.011 & -0.676 & -0.736 \\ 0.814 & -0.433 & 0.386 \\ 0.58 & 0.596 & -0.556 \end{pmatrix} \quad S_4^T := S_4^{-1}$$
$$|S_4| = -1 \quad \text{Eq [32a]}$$

This means that lengths of the transformed C-H bonds are conserved:

**Exercise 23** *Show by demonstration that bond lengths in methane are conserved upon  $S_4$  operations.*

## **Inversion and Dihedral Mirror Plane Reflections of Benzene Molecule**

### ***Molecular coordinate Data***

The matrix  $C_6H_6$  consists of coordinates of 6 carbon atoms (the first 6 rows), and 6 hydrogen atoms (bottom 6 rows). The matrix  $AC_6H_6$  consists of coordinates of only 6 carbon atoms. The units are in Angstroms.

$$\begin{array}{c}
 \begin{array}{ccc}
 \mathbf{x} & \mathbf{y} & \mathbf{z} \\
 \left( \begin{array}{ccc}
 -2.17194 & -0.21073 & 0 \\
 -2.17195 & 1.18422 & 0 \\
 -0.96378 & 1.88179 & 0 \\
 0.24432 & 1.18424 & 0 \\
 0.24432 & -0.21076 & 0 \\
 -0.96380 & -0.90831 & 0 \\
 -3.12437 & -0.76026 & 0 \\
 -3.12437 & 1.73375 & 0 \\
 -0.96345 & 2.98135 & 0 \\
 1.19641 & 1.73434 & 0 \\
 1.19641 & -0.76087 & 0 \\
 -0.96346 & -2.00787 & 0
 \end{array} \right) \\
 \text{C6H6} :=
 \end{array}
 &
 \begin{array}{c}
 \begin{array}{ccc}
 \mathbf{x} & \mathbf{y} & \mathbf{z} \\
 \left( \begin{array}{ccc}
 -2.17194 & -0.21073 & 0 \\
 -2.17195 & 1.18422 & 0 \\
 -0.96378 & 1.88179 & 0 \\
 0.24432 & 1.18424 & 0 \\
 0.24432 & -0.21076 & 0 \\
 -0.96380 & -0.90831 & 0
 \end{array} \right) \\
 \text{AC6H6} :=
 \end{array}
 &
 \begin{array}{c}
 \text{C1} \\
 \text{C2} \\
 \text{C3} \\
 \text{C4} \\
 \text{C5} \\
 \text{C6}
 \end{array}
 \end{array}
 \end{array}
 \quad \text{Eq [33]}$$

$$\begin{array}{c}
 \begin{array}{ccc}
 \mathbf{x} & \mathbf{y} & \mathbf{z} \\
 \left( \begin{array}{ccc}
 -2.17194 & -0.21073 & 0 \\
 -2.17195 & 1.18422 & 0 \\
 -0.96378 & 1.88179 & 0 \\
 0.24432 & 1.18424 & 0 \\
 0.24432 & -0.21076 & 0 \\
 -0.96380 & -0.90831 & 0 \\
 -2.17194 & -0.21073 & 0
 \end{array} \right) \\
 \text{BC6H6} :=
 \end{array}
 &
 \begin{array}{c}
 \text{C1} \\
 \text{C2} \\
 \text{C3} \\
 \text{C4} \\
 \text{C5} \\
 \text{C6} \\
 \text{C1}
 \end{array}
 \end{array}
 \quad \text{Eq [34]}$$

$i := 0..2 \quad \text{benzene}_i := \text{BC6H6}^{(i)}$

**Plotting benzene molecule**

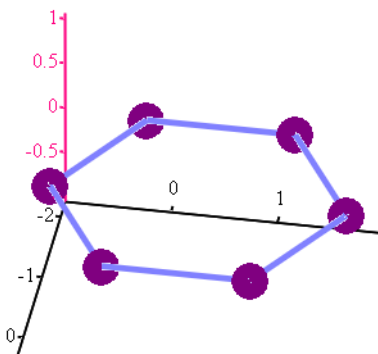


Fig 8 The benzene molecule.

benzene

The six displacement vectors from a carbon atom to one of its nearest neighbors are given by:

$$j := 0..4$$

$$\begin{aligned} r^{\langle j \rangle} &:= (\text{AC6H6}^T)^{\langle j+1 \rangle} - (\text{AC6H6}^T)^{\langle j \rangle} \\ r^{\langle 5 \rangle} &:= (\text{AC6H6}^T)^{\langle 0 \rangle} - (\text{AC6H6}^T)^{\langle 5 \rangle} \end{aligned} \quad \text{Eq [35]}$$

$$r^T = \begin{pmatrix} -10 \times 10^{-6} & 1.395 & 0 \\ 1.208 & 0.698 & 0 \\ 1.208 & -0.698 & 0 \\ 0 & -1.395 & 0 \\ -1.208 & -0.698 & 0 \\ -1.208 & 0.698 & 0 \end{pmatrix} \quad \text{Eq [36]}$$

$$r = \begin{pmatrix} -10 \times 10^{-6} & 1.208 & 1.208 & 0 & -1.208 & -1.208 \\ 1.395 & 0.698 & -0.698 & -1.395 & -0.698 & 0.698 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [37]}$$

### Angles between C-C bonds

**Exercise 24** Find the bond angles between two adjacent bonds and bond lengths for each C-C bonds. An example for the angle between  $r^{\langle 1 \rangle}$  and  $r^{\langle 2 \rangle}$  is shown as follows:

$$\text{angle}[r^{\langle 1 \rangle}, (-r)^{\langle 2 \rangle}] = 119.997 \text{ deg} \quad \text{Eq [38]}$$

Note: In order to get the proper angle between 2 adjacent C-C bonds, the sign (hence the direction) of one of the vectors is reversed. Draw the vectors,  $r^{\langle 0 \rangle}$ ,  $r^{\langle 1 \rangle}$ , etc that is defined in Eq.[35] including the directions of vectors with an arrow from the starting point to the end points. The reason for the sign reversal in Eq.[38] is to make sure that the angle measured between 2 adjacent bonds are emanating from the same carbon atoms and pointing to the neighboring atoms. Repeat the same calculations for other adjacent bonds.

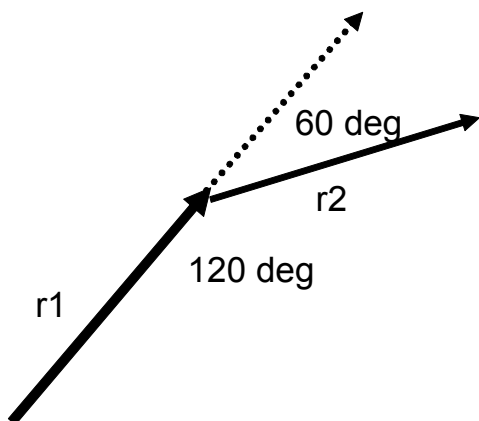


Fig 9 A diagram to illustrate calculation of the angle between two vectors.

The diagram on the left illustrates why this is the case. The angle between vectors r1 and r2 is 60 deg, while the angle between -r1 and r2 is 120 deg. To get the proper angle for two adjacent C-C bonds, adjacent vectors must emanate from the same point and pointing to the neighboring adjacent atoms.

## Inversion

To find the origin of the benzene ring, we must add up all six coordinates and divide the sum by 6. Here is the coordinates of the center of the ring:

$$\text{origin} := \frac{1}{6} \cdot \sum_{j=0}^5 (\text{AC6H6}^T)^{\langle j \rangle} \quad \bullet = \blacksquare \quad \text{Eq [39]}$$

Define new benzene coordinates with o as the origin

j := 0..5

$$\text{NewC6H6}^{\langle j \rangle} := (\text{AC6H6}^T)^{\langle j \rangle} - \text{origin} \quad \text{Eq [40]}$$

In Eq.[40], the x-coordinates of each carbon atom is displayed on the first row, y-coordinates on the second row, z-coordinates on the third row.

$$\text{NewC6H6} = \begin{pmatrix} -1.208 & -1.208 & 2.5 \times 10^{-5} & 1.208 & 1.208 & 5 \times 10^{-6} \\ -0.697 & 0.697 & 1.395 & 0.697 & -0.698 & -1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [41]}$$

$$\text{NewC6H6} := \begin{pmatrix} -1.208 & -1.208 & 0 & 1.208 & 1.208 & 0 \\ -0.697 & 0.697 & 1.395 & 0.697 & -0.698 & -1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

**Exercise 25** Assign  $x$ ,  $y$ ,  $z$  and carbon numbers (or bond numbers) to the matrices in Eq [41]

$$\text{Applying inversion operator} \quad \text{inver} := \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{Eq [42]}$$

$$\text{inver} \cdot \text{NewC6H6} = \begin{pmatrix} 1.208 & 1.208 & 0 & -1.208 & -1.208 & 0 \\ 0.697 & -0.697 & -1.395 & -0.697 & 0.698 & 1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [43]}$$

Compare this with NewC6H6

$$\text{NewC6H6} = \begin{pmatrix} -1.208 & -1.208 & 0 & 1.208 & 1.208 & 0 \\ -0.697 & 0.697 & 1.395 & 0.697 & -0.698 & -1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [41]}$$

The two matrices,  $\text{inver} \cdot \text{NewC6H6}$  and  $\text{NewC6H6}$ , have the same vectors, but interchanged. They are indistinguishable.

### **Dihedral Reflection Mirror Planes**

Benzene has 3  $\sigma_d$  planes for which  $\sigma_d$  operations will return the molecule to itself. We shall see what these operations do. To define one  $\sigma$ , we have to find mid-point for C1-C2; C4-C5. Then define the axis in terms of this vector connecting two mid-points.

$$\text{mid12} := \frac{1}{2} \cdot (\text{NewC6H6}^{\langle 1 \rangle} + \text{NewC6H6}^{\langle 0 \rangle}) \quad \text{mid12} = \begin{pmatrix} -1.208 \\ 0 \\ 0 \end{pmatrix} \quad \text{Eq [42]}$$

$$\text{mid45} := \frac{1}{2} \cdot (\text{NewC6H6}^{\langle 3 \rangle} + \text{NewC6H6}^{\langle 4 \rangle})$$

$$\text{mid45} = \begin{pmatrix} 1.208 \\ -5 \times 10^{-4} \\ 0 \end{pmatrix} \quad \text{mid45} := \begin{pmatrix} 1.208 \\ 0 \\ 0 \end{pmatrix}$$

$$\sigma_{d1} := \frac{\text{mid45} - \text{mid12}}{|\text{mid45} - \text{mid12}|}$$

$$\text{Refl}(\sigma_{d1}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{Is Refl}(\sigma_{d1}) \text{ a Hermitian matrix?}$$

$$\text{Refl}(\sigma_{d1}) \cdot \text{NewC6H6} = \begin{pmatrix} 1.208 & 1.208 & 0 & -1.208 & -1.208 & 0 \\ -0.697 & 0.697 & 1.395 & 0.697 & -0.698 & -1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [43]}$$

$$\text{NewC6H6} = \begin{pmatrix} -1.208 & -1.208 & 0 & 1.208 & 1.208 & 0 \\ -0.697 & 0.697 & 1.395 & 0.697 & -0.698 & -1.395 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Eq [41]}$$

**Exercise 26** Follow the procedures shown above and find axes of the other two dihedral reflection planes. Find the matrices for these planes.

**Mastery Exercise:** In the ammonia molecule example, HyperChem was well set-up such that all three H atoms had the same z-coordinates (Look at Eq. [18]). What happens if the HyperChem was not well set up and all three H-atoms do not have the same z-coordinates as shown in the following matrix [Eq 44].

	N	H1	H2	H3	
NH3 :=	-0.84312	0.08236	-0.9301	-0.9301	x
	-0.002139	0.37793	-0.5874	-0.5874	y
	0.39744	0.39744	1.2047	-0.4098	z

Eq [44]

Define C3 matrix for this new coordinate system.

**Acknowledgement** The author thanks Mr. Tom Gutman from Mathcad users' forum providing elegant rotational and reflection operators for any axis. The author also thanks Drs. Louis Kijewski and Theresa Julia Zielinski of Monmouth University for useful discussions.

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