8-4-2006

Rotations, Precursor to Rotational Spectroscopy, and Group Theory

Carl W. David

University of Connecticut, Carl.David@uconn.edu

Follow this and additional works at: http://digitalcommons.uconn.edu/chem_educ

Rotations, Precursor to Rotational Spectroscopy, and Group Theory

C. W. David
Department of Chemistry
University of Connecticut
Storrs, Connecticut 06269-3060
(Dated: August 4, 2006)

I. SYNOPSIS

Rotations, in two and three dimensions, forms the basis for parts of group theory as applied to chemistry, as well as the basis upon which angular momentum and rigid body rotations are treated. This elementary discussion introduces the concepts (hopefully) gently.

II. PLANAR ROTATIONS

The consequences of studying rotations are so enormous that one can not begin to outline all of the subjects which will touch this one. Not only will we deal with rotational spectroscopy and rotational fine structure of other spectroscopies, but we will deal with magnetic resonance, group theory, spin, etc., all tied to concepts discussed here.

We start with a two dimensional rotation study in Cartesian coordinates, i.e., one in which the set $\{x,y\}$ is transformed into the set $\{x',y'\}$, where both sets are Cartesian, but one set is rotated relative to the other. x' is perpendicular to y', just as x is perpendicular to y. The two coordinate systems share a common origin, so one is twisted relative to the other, that's all.

We will see from the Figure 1 that

$$x' = x \cos\alpha + y \sin\alpha \qquad (2.1)$$

and

$$y' = -x \sin\alpha + y \cos\alpha \qquad (2.2)$$

by virtue of elementary trigonometry. This rotation is known as a radius preserving transformation, since the distance from the origin to P(x,y) is the same as the distance from the origin to P(x',y'). It is common to write this transformation set of equations as

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \otimes \begin{pmatrix} x \\ y \end{pmatrix}$$

which compresses the notation into a column vector being equal to the product of a transformation (rotation) matrix and another column vector.

To see where this comes from, consider the simultaneous equations

$$x' = r \cos\beta = r \cos(\gamma - \alpha) \qquad (2.3)$$
$$y' = r \sin\beta = r \sin(\gamma - \alpha) \qquad (2.4)$$

which becomes

$$x' = r \cos(\gamma - \alpha) = r \cos\gamma \cos\alpha - r \sin(-\alpha) \sin\gamma \quad (2.5)$$
$$y' = r \sin(\gamma - \alpha) = r \sin\gamma \cos\alpha + r \sin(-\alpha) \cos\gamma \quad (2.6)$$

where we emphasize that the sine is odd, while the cosine is even. Remembering what $r \cos\gamma$ and $r \sin\gamma$ are, we have

$$x' = x \cos\alpha + y \sin\alpha \qquad (2.7)$$
$$y' = -x \sin\alpha + y \cos\alpha \qquad (2.8)$$

These last two equations are identical to Equations 2.1 and 2.2.

We will see that this compression of notation extends to 3 and beyond dimensions, allowing a compact notation to standard for an enormous number of individual (similar) equations.

When we have two rotations (see Figure 2), one after the other, we would have x go to x' (using an angle α_1) and then go to x"(using another angle, relative to x', of α_2), we can write this as

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\alpha_1 & \sin\alpha_1 \\ -\sin\alpha_1 & \cos\alpha_1 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \end{pmatrix} \qquad (2.9)$$

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\alpha_2 & \sin\alpha_2 \\ -\sin\alpha_2 & \cos\alpha_2 \end{pmatrix} \otimes \begin{pmatrix} x' \\ y' \end{pmatrix} \qquad (2.10)$$

which means that there is an overall rotation from x' to x" directly,

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\alpha_3 & \sin\alpha_3 \\ -\sin\alpha_3 & \cos\alpha_3 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \end{pmatrix} \qquad (2.11)$$

where α_3 is the overall angle of rotation. What is the relation between α_1, α_2, and α_3?

Substituting Equation 2.9 into Equation 2.10, and equating the results to Equation 2.12 we obtain

$$\begin{pmatrix} \cos\alpha_1 & \sin\alpha_1 \\ -\sin\alpha_1 & \cos\alpha_1 \end{pmatrix} \otimes \begin{pmatrix} \cos\alpha_2 & \sin\alpha_2 \\ -\sin\alpha_2 & \cos\alpha_2 \end{pmatrix}$$
$$= \begin{pmatrix} \cos\alpha_3 & \sin\alpha_3 \\ -\sin\alpha_3 & \cos\alpha_3 \end{pmatrix} \quad (2.12)$$

which *defines* matrix multiplication.

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\alpha_1 & \sin\alpha_1 \\ -\sin\alpha_1 & \cos\alpha_1 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \end{pmatrix}$$
$$= \begin{pmatrix} x \cos\alpha_1 + y \sin\alpha_1 \\ -x \sin\alpha_1 + y \cos\alpha_1 \end{pmatrix} \quad (2.13)$$

which means that we can substitute the primed values into the second rotation

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\alpha_2 & \sin\alpha_2 \\ -\sin\alpha_2 & \cos\alpha_2 \end{pmatrix} \otimes \begin{pmatrix} x' \\ y' \end{pmatrix} \qquad (2.14)$$

giving

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\alpha_2 & \sin\alpha_2 \\ -\sin\alpha_2 & \cos\alpha_2 \end{pmatrix} \otimes \begin{pmatrix} x\cos\alpha_1 + y\sin\alpha_1 \\ -x\sin\alpha_1 + y\cos\alpha_1 \end{pmatrix}$$
$$= \begin{pmatrix} (x\cos\alpha_1 + y\sin\alpha_1)\cos\alpha_2 + (-x\sin\alpha_1 + y\cos\alpha_1)\sin\alpha_2 \\ (x\cos\alpha_1 + y\sin\alpha_1)(-\sin\alpha_2) + (-x\sin\alpha_1 + y\cos\alpha_1)\cos\alpha_2 \end{pmatrix} \qquad (2.15)$$

which means that there is an overall rotation from x' to x" directly,

$$\begin{pmatrix} x\cos\alpha_1\cos\alpha_2 + y\sin\alpha_1\cos\alpha_2 - x\sin\alpha_1\sin\alpha_2 + y\cos\alpha_1\sin\alpha_2 \\ -\sin\alpha_2 x\cos\alpha_1 - y\sin\alpha_1\sin\alpha_2 - x\sin\alpha_1\cos\alpha_2 + y\cos\alpha_1\cos\alpha_2 \end{pmatrix}$$

which we rewrite as

$$\begin{pmatrix} x(\cos\alpha_1\cos\alpha_2 - \sin\alpha_1\sin\alpha_2) + y(\sin\alpha_1\cos\alpha_2 + \cos\alpha_1\sin\alpha_2) \\ x(-\sin\alpha_2\cos\alpha_1 - \sin\alpha_1\cos\alpha_2) - y(\sin\alpha_1\sin\alpha_2 - y\cos\alpha_1\cos\alpha_2) \end{pmatrix} \qquad (2.16)$$

which is, using the sum and differences of sines and cosines of angles (DeMoivre, again),

$$\begin{pmatrix} x\cos(\alpha_1 + \alpha_2) + y\sin(\alpha_1 + \alpha_2) \\ -x\sin(\alpha_1 + \alpha_2) + y\cos(\alpha_1 + \alpha_2) \end{pmatrix} = \begin{pmatrix} x\cos\alpha_3 + y\sin\alpha_3 \\ -x\sin\alpha_3 + y\cos\alpha_3 \end{pmatrix}$$

which works, since $\alpha_1 + \alpha_2 = \alpha_3$ in actuality. We have therefore shown that Equation 2.10 and Equation 2.11 are equivalent to

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\alpha_2 & \sin\alpha_2 \\ -\sin\alpha_2 & \cos\alpha_2 \end{pmatrix} \otimes \begin{pmatrix} x' \\ y' \end{pmatrix}$$
$$= \begin{pmatrix} x(\cos\alpha_1\cos\alpha_2 - \sin\alpha_1\sin\alpha_2) + y(\sin\alpha_1\cos\alpha_2 + \cos\alpha_1\sin\alpha_2) \\ x(-\sin\alpha_2\cos\alpha_1 - \sin\alpha_1\cos\alpha_2) - y(\sin\alpha_1\sin\alpha_2 - y\cos\alpha_1\cos\alpha_2) \end{pmatrix} \qquad (2.17)$$

III. THREE DIMENSIONAL ROTATIONS

When we turn to three dimensions (and beyond) things get harder to visualize. Consider an arbitrary rotation in 3-dimensional space, as shown in the accompanying figure: This corresponds to rotating first about the z-axis, and then rotating about the x-axis (for example). Notice the "and then" part of the last sentence. It is a dead giveaway that the order in which we do these rotations is important

> "We are entering the region of non-commutative algebra, where the order of operations becomes important. 7 times 6 is the same as 6 times 7, but rotate about x and then rotate about z is not, repeat not, the same as rotate about z and then rotate about x."

In our example, we are doing two compounded planar rotations to achieve an overall three dimensional rota-

tion, i.e., first, we rotate about the z-axis, so the rotation matrix for this rotation is

$$\begin{pmatrix} \cos\vartheta_1 & \sin\vartheta_1 & 0 \\ -\sin\vartheta_1 & \cos\vartheta_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which operates on a column vector of coordinates:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

resulting in a new column vector of transformed coordinates:

$$\begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix}$$

which is usually written as a single equation:

$$\begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix} = \begin{pmatrix} \cos\vartheta_1 & \sin\vartheta_1 & 0 \\ -\sin\vartheta_1 & \cos\vartheta_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad (3.1)$$

One sees explicitly that $z^i = z$, i.e., the "1" in the 3,3 position of the rotation matrix guarantees that the rotation about the z-axis preserves values of z!

Let us now rotate from the new coordinate system, this time about the x^i-axis:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\vartheta_2 & \sin\vartheta_2 \\ 0 & -\sin\vartheta_2 & \cos\vartheta_2 \end{pmatrix} \otimes \begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix} \qquad (3.2)$$

Obviously (substituting Equation 3.2 into Equation 3.1), this is

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\vartheta_2 & \sin\vartheta_2 \\ 0 & -\sin\vartheta_2 & \cos\vartheta_2 \end{pmatrix} \otimes \begin{pmatrix} \cos\vartheta_1 & \sin\vartheta_1 & 0 \\ -\sin\vartheta_1 & \cos\vartheta_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Notice the ordering, i.e., the first rotation is "to the right" of the second rotation in terms of the ordering of the rotation matrices. The overall rotation, taking the matrix product explicitly, is

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\vartheta_1 & \sin\vartheta_1 & 0 \\ -\cos\vartheta_2 \sin\vartheta_1 & \cos\vartheta_2 \cos\vartheta_1 & \sin\vartheta_2 \\ \sin\vartheta_2 \sin\vartheta_1 & -\sin\vartheta_2 \cos\vartheta_1 & \cos\vartheta_2 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Notice the lack of main diagonal symetry here.

IV.   EQUIVALENT SINGLE ROTATION AXIS

Is there an axis about which *this* composite rotation could have taken place in one fell swoop? Physically, we know this is true, there does exist such an axis, but the question is, where is it?

The answer is, that points on this axis do not change their coordinate values during the rotation, i.e.,

$$\begin{pmatrix} x_a \\ y_a \\ z_a \end{pmatrix}$$

when substituted into the overall rotation equation, is the same before and after rotation.

$$\begin{pmatrix} x_a \\ y_a \\ z_a \end{pmatrix} = \begin{pmatrix} \cos\vartheta_1 & \sin\vartheta_1 & 0 \\ -\cos\vartheta_2 \sin\vartheta_1 & \cos\vartheta_2 \cos\vartheta_1 & \sin\vartheta_2 \\ \sin\vartheta_2 \sin\vartheta_1 & -\sin\vartheta_2 \cos\vartheta_1 & \cos\vartheta_2 \end{pmatrix} \otimes \begin{pmatrix} x_a \\ y_a \\ z_a \end{pmatrix}$$

Take as an example the vector (1,2,3), i.e.

$$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$$

and let us rotate by 30 degrees about the z axis. We obtain

$$\begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix} = \begin{pmatrix} \cos 30 & \sin 30 & 0 \\ -\sin 30 & \cos 30 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

which is

$$\begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} \rightarrow \begin{pmatrix} \frac{\sqrt{3}}{2} + 1 \\ -\frac{1}{2} + \sqrt{3} \\ 3 \end{pmatrix}$$

rotating 30° about the new x-axis, so

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix} \otimes \begin{pmatrix} \frac{\sqrt{3}}{2} + 1 \\ -\frac{1}{2} + \sqrt{3} \\ 3 \end{pmatrix}$$

which is

$$\begin{pmatrix} \frac{\sqrt{3}}{2}+1 \\ \frac{\sqrt{3}}{2}\left(-\frac{1}{2}+\sqrt{3}\right) \\ \frac{1}{2}\left(-\frac{1}{2}+\sqrt{3}\right)+3\left(\frac{\sqrt{3}}{2}\right) \end{pmatrix} = \begin{pmatrix} 1.866 \\ 1.067 \\ 3.214 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix} \otimes \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{3}{4} & \frac{1}{2} \\ \frac{1}{4} & -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{2} \end{pmatrix} = \begin{pmatrix} 0.866 & 0.5 & 0 \\ -0.433 & 0.75 & 0.5 \\ 0.25 & -0.433 & 0.866 \end{pmatrix}$$

If one diagonalizes this last matrix, one obtains three eigenvalues, two of which are imaginary pairs, one one of which is "1", within numerical accuracy *vide supra*. The eigenfunction associated with that latter eigenvalue is

$$\begin{pmatrix} 0.6987 \\ 0.1872 \\ 0.6987 \end{pmatrix}$$

$$\begin{pmatrix} 0.866 & 0.5 & 0 \\ -0.433 & 0.75 & 0.5 \\ 0.25 & -0.433 & 0.866 \end{pmatrix} \otimes \begin{pmatrix} 0.6987 \\ 0.1872 \\ 0.6987 \end{pmatrix} = \begin{pmatrix} 0.6987 \times 0.866 + 0.5 \times 0.1872 \\ -0.433 \times 0.6987 + 0.75 * 0.1872 + 0.5 \times 0.6987 \\ 0.25 \times 0.6987 - 0.433 \times 0.1872 + 0.866 \times 0.6987 \end{pmatrix}$$

which is, lo and behold,

$$\begin{pmatrix} 0.6987 \\ 0.1872 \\ 0.6987 \end{pmatrix}$$

Here is some Maple code which accomplishes the diagonalization discussed above.

```
restart;
```

The overall rotation matrix is

and when one operates on this eigenfunction wtih the original matrix one obtains

```
with(linalg):
t1 := evalf(sqrt(3)/2);
t2 := evalf(sqrt(3)/4);
A := array([[t1,1/2,0],[-t2,3/4,1/2],[1/4,-t2,t1]]);
evalf(Eigenvals(A));
vecs := evalf(eigenvectors(A));
vlist := vecs[3];
s := vlist[3];
```
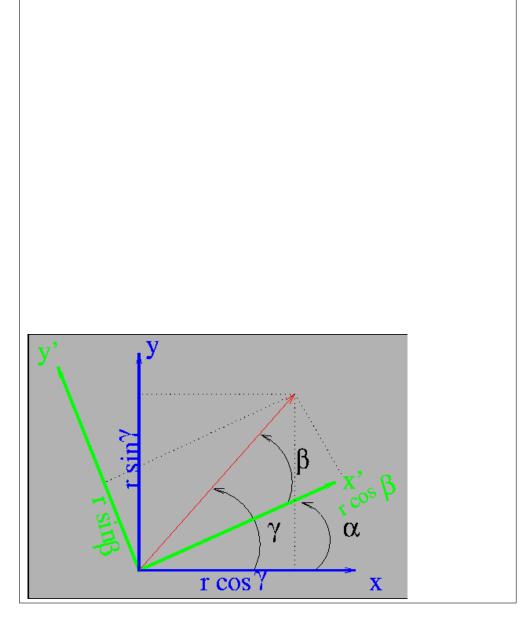
FIG. 1: A planar rotation, and the relationship between the projections of the radius onto the coordinate systems before and after rotation.
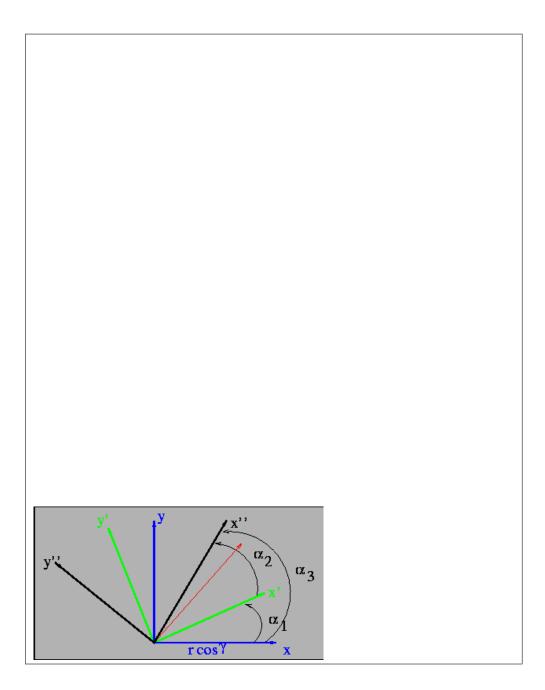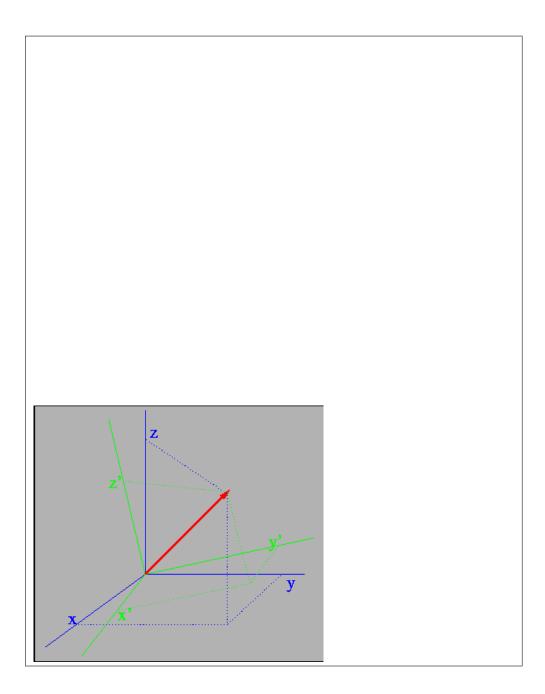
FIG. 2: Two compounded planar rotations

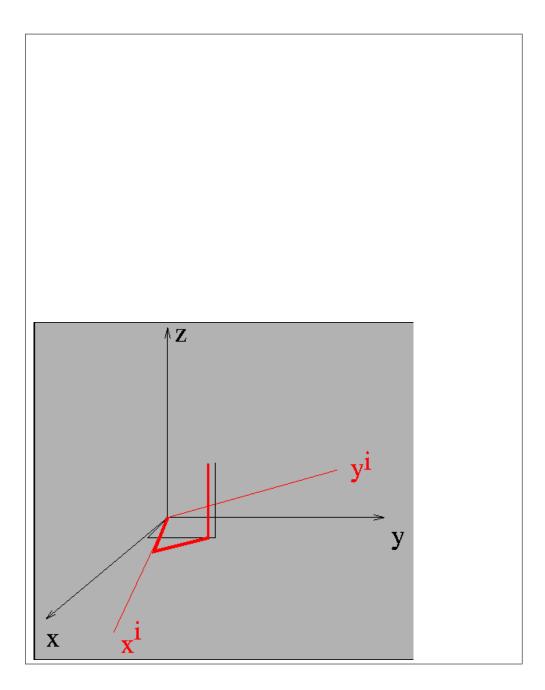FIG. 3: Two compounded planar rotations about different axes giving rise to a three-dimensional rotation.

FIG. 4: After the first rotation (30°).