\[ \frac{h^2}{2\mu \sqrt{64\pi}} \frac{1}{a_0^{3/2}} \frac{r}{a_0} e^{-r^2a_0} e^{i\phi} \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \cos \theta) \]

\[ \frac{h^2}{2\mu \sqrt{64\pi}} \frac{1}{a_0^{3/2}} \frac{r}{a_0} e^{-r^2a_0} e^{i\phi} \frac{1}{r^2 \sin \theta} (\cos^2 \theta - \sin^2 \theta) \]

Partial differentiation with respect to \( \phi \) is also not difficult, because the terms that depend on \( r \) and \( \theta \) are constant:

\[ \frac{h^2}{2\mu \sqrt{64\pi}} \frac{1}{a_0^{3/2}} \frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \phi^2} \left( e^{-r^2a_0} \sin \theta e^{i\phi} \right) \]

\[ \frac{h^2}{2\mu \sqrt{64\pi}} \frac{1}{a_0^{3/2}} \frac{1}{r^2} \left( \frac{\partial^2 e^{i\phi}}{\partial \phi^2} \right) \]

\[ \frac{h^2}{2\mu \sqrt{64\pi}} \frac{1}{a_0^{3/2}} \frac{r}{a_0} e^{-r^2a_0} \frac{1}{r^2} \left( e^{i\phi} \right) \]

### A.7 Working with Determinants

A determinant of \( n \)th order is a square \( n \times n \) array of numbers symbolically enclosed by vertical lines. A fifth-order determinant is shown here with the conventional indexing of the elements of the array:

\[
\begin{vmatrix}
  a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\
  a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\
  a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \\
  a_{41} & a_{42} & a_{43} & a_{44} & a_{45} \\
  a_{51} & a_{52} & a_{53} & a_{54} & a_{55}
\end{vmatrix}
\]  

(A.64)

A 2 \( \times \) 2 determinant has a value that is defined in Equation (A.65). It is obtained by multiplying the elements in the diagonal connected by a line with a negative slope and subtracting from this the product of the elements in the diagonal connected by a line with a positive slope.

\[
\begin{vmatrix}
  a_{11} & a_{12} \\
  a_{21} & a_{22}
\end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}
\]

(A.65)

The value of a higher order determinant is obtained by expanding the determinant in terms of determinants of lower order. This is done using the method of cofactors. We illustrate the use of method of cofactors by reducing a 3 \( \times \) 3 determinant to a sum of 2 \( \times \) 2 determinants. Any row or column can be used in the reduction process. We use the first row of the determinant in the reduction. The recipe is spelled out in this equation:

\[
\begin{vmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{vmatrix} = (-1)^{1+1}a_{11} \begin{vmatrix}
  a_{22} & a_{23} \\
  a_{32} & a_{33}
\end{vmatrix} + (-1)^{1+2}a_{12} \begin{vmatrix}
  a_{21} & a_{23} \\
  a_{31} & a_{33}
\end{vmatrix}
\]

\[
+ (-1)^{1+3}a_{13} \begin{vmatrix}
  a_{21} & a_{22} \\
  a_{31} & a_{32}
\end{vmatrix}
\]

(A.66)

Each term in the sum results from the product of one of the three elements of the first row, \((-1)^{m+n}\), where \( m \) and \( n \) are the indices of the row and column designating the element.
respectively, and the $2 \times 2$ determinant obtained by omitting the entire row and column to which the element used in the reduction belongs. The product $(-1)^{m+n}$ and the $2 \times 2$ determinant are called the cofactor of the element used in the reduction. For example, the value of the following $3 \times 3$ determinant is found using the cofactors of the second row:

\[
\begin{vmatrix}
1 & 3 & 4 \\
2 & -1 & 6 \\
-1 & 7 & 5 \\
\end{vmatrix} = (-1)^{2+1} \begin{vmatrix} 3 & 4 \\
7 & 5 \\
\end{vmatrix} + (-1)^{2+2}(-1) \begin{vmatrix} 1 & 4 \\
-1 & 5 \\
\end{vmatrix} + (-1)^{2+3}6 \begin{vmatrix} 1 & 3 \\
-1 & 7 \\
\end{vmatrix} \\
= -1 \times 2 \times (-13) + 1 \times (-1) \times 9 + (-1) \times 6 \times 10 = -43
\]

If the initial determinant is of a higher order than 3, multiple sequential reductions as outlined earlier will reduce it in order by one in each step until a sum of $2 \times 2$ determinants is obtained.

The main usefulness for determinants is in solving a system of linear equations. Such a system of equations is obtained in evaluating the energies of a set of molecular orbitals obtained by combining a set of atomic orbitals. Before illustrating this method, we list some important properties of determinants that we will need in solving a set of simultaneous equations.

**Property I**  The value of a determinant is not altered if each row in turn is made into a column or vice versa as long as the original order is kept. By this we mean that the $n$th row becomes the $n$th column. This property can be illustrated using $2 \times 2$ and $3 \times 3$ determinants:

\[
\begin{vmatrix}
2 & 1 \\
3 & -1 \\
\end{vmatrix} = -5 \quad \text{and} \quad \begin{vmatrix} 1 & 3 & 4 \\
2 & -1 & 6 \\
-1 & 7 & 5 \\
\end{vmatrix} = -43
\]

**Property II**  If any two rows or columns are interchanged, the sign of the value of the determinant is changed. For example,

\[
\begin{vmatrix}
2 & 1 \\
3 & -1 \\
\end{vmatrix} = -5, \text{ but } \begin{vmatrix} 1 & 2 \\
-1 & 3 \\
\end{vmatrix} = +5 \quad \text{and} \quad \begin{vmatrix} 1 & 3 & 4 \\
2 & -1 & 6 \\
-1 & 7 & 5 \\
\end{vmatrix} = -43, \text{ but } \begin{vmatrix} 1 & 3 & 4 \\
2 & -1 & 6 \\
-1 & 7 & 5 \\
\end{vmatrix} = +43
\]

**Property III**  If two rows or columns of a determinant are identical, the value of the determinant is zero. For example,

\[
\begin{vmatrix} 2 & 1 \\
2 & 1 \\
\end{vmatrix} = 2 - 2 = 0 \quad \text{and} \quad \begin{vmatrix} 1 & 1 & 4 \\
2 & 2 & 6 \\
-1 & -1 & 5 \\
\end{vmatrix} = (-1)^{2+1} \begin{vmatrix} 1 & 4 \\
-1 & 5 \\
\end{vmatrix} + (-1)^{2+2}2 \begin{vmatrix} 1 & 4 \\
-1 & 5 \\
\end{vmatrix} \\
+ (-1)^{2+3}6 \begin{vmatrix} 1 \ \\
-1 \\
\end{vmatrix} \\
= -1 \times 2 \times 9 + 1 \times 2 \times 9 + (-1) \times 6 \times 0 = 0
\]

**Property IV**  If each element of a row or column is multiplied by a constant, the value of the determinant is multiplied by that constant. For example,

\[
\begin{vmatrix} 2 & 1 \\
3 & -1 \\
\end{vmatrix} = -5 \quad \text{and} \quad \begin{vmatrix} 8 & 4 \\
3 & -1 \\
\end{vmatrix} = -20 \quad \text{and} \quad \begin{vmatrix} 1 & 2 & -1 \\
3 & -1 & 7 \\
4 & 6 & 5 \\
\end{vmatrix} = -43 \quad \text{and} \quad \begin{vmatrix} 1 & 3 \sqrt{2} & 4 \\
2 & - \sqrt{2} & 6 \\
-1 & 7 \sqrt{2} & 5 \\
\end{vmatrix} = -43 \sqrt{2}
\]

**Property V**  The value of a determinant is unchanged if a row or column multiplied by an arbitrary number is added to another row or column. For example,
\[
\begin{vmatrix}
2 & 1 \\
3 & -1
\end{vmatrix} = \begin{vmatrix}
2+1 & 1 \\
3-1 & -1
\end{vmatrix} = \begin{vmatrix}
2 & 1 \\
3 & -1
\end{vmatrix} = -5 \text{ and }
\]
\[
\begin{vmatrix}
1 & 3 & 4 \\
2 & -1 & 6 \\
-1 & 7 & 5
\end{vmatrix} = \begin{vmatrix}
1 & 3 & 4 \\
2 & -1 & 6 \\
\end{vmatrix} = -43
\]

How are determinants useful? This question can be answered by illustrating how determinants can be used to solve a set of linear equations:

\[
x + y + z = 10 \\
3x + 4y - z = 12 \\
x - 2y + 5z = 26
\]

This set of equations is solved by first constructing the \(3 \times 3\) determinant that is the array of the coefficients of \(x, y,\) and \(z:\)

\[
\mathbf{D}_{\text{coefficients}} = \begin{vmatrix}
1 & 1 & 1 \\
3 & 4 & -1 \\
-1 & 2 & 5
\end{vmatrix}
\]

Now imagine that we multiply the first column by \(x\). This changes the value of the determinant as stated in Property IV:

\[
\begin{vmatrix}
1x & 1 & 1 \\
3x & 4 & -1 \\
-1x & 2 & 5
\end{vmatrix} = x\mathbf{D}_{\text{coefficients}}
\]

We next add to the first column of \(x\mathbf{D}_{\text{coefficients}}\) the second column of \(\mathbf{D}_{\text{coefficients}}\) multiplied by \(y\), and the third column multiplied by \(z\). According to Properties IV and V, the value of the determinant is unchanged. Therefore,

\[
\mathbf{D}_{e1} = \begin{vmatrix}
1 & 1 & 1 \\
3 & 4 & -1 \\
-1 & 2 & 5
\end{vmatrix} = \begin{vmatrix}
x + y + z & 1 & 1 \\
x + 4y - z & 4 & -1 \\
x + 2y + 5z & 2 & 5
\end{vmatrix} = x\mathbf{D}_{\text{coefficients}}
\]

To obtain the third determinant in the previous equation, the individual equations in Equation (A.67) are used to substitute the constants for the algebraic expression in the preceding determinants. From the previous equation, we conclude that

\[
x = \frac{\mathbf{D}_{e1}}{\mathbf{D}_{\text{coefficients}}} = \frac{10 \quad 1 \quad 1}{12 \quad 4 \quad -1} = \frac{26 \quad 2 \quad 5}{1 \quad 1 \quad 1} = \frac{3 \quad 4 \quad -1}{-1 \quad 2 \quad 5}
\]

To determine \(y\) and \(z\), the exact same procedure can be followed, but we substitute instead in columns 2 and 3, respectively. The first step in each case is to multiply all elements of the second (third) row by \(y(z)\). If we do so, we obtain the determinants \(\mathbf{D}_{e2}\) and \(\mathbf{D}_{e3}\):

\[
\mathbf{D}_{e2} = \begin{vmatrix}
1 & 10 & 1 \\
3 & 12 & -1 \\
-1 & 26 & 5
\end{vmatrix} \quad \text{and} \quad \mathbf{D}_{e3} = \begin{vmatrix}
1 & 1 & 10 \\
3 & 4 & 12 \\
-1 & 2 & 26
\end{vmatrix}
\]

and we conclude that
This method of solving a set of simultaneous linear equations is known as Cramer's method.

If the constants in the set of equations are all zero, as in Equations A.71a and A.71b,

\[
x + y + z = 0
\]
\[
3x + 4y - z = 0
\]
\[
-x + 2y + 5z = 0
\]

the determinants \( D_{\text{coefficients}} \), \( D_{2} \), and \( D_{3} \) all have the value zero. An obvious set of solutions is \( x = 0 \), \( y = 0 \), and \( z = 0 \). For most problems in physics and chemistry, this set of solutions is not physically meaningful and is referred to as the set of trivial solutions. A set of nontrivial solutions only exists if the equation \( D_{\text{coefficients}} = 0 \) is satisfied. There is no nontrivial solution to the set of Equation A.71a because \( D_{\text{coefficients}} \neq 0 \). There is a set of nontrivial solutions to the set of Equations A.71b, because \( D_{\text{coefficients}} = 0 \) in this case.

Determinants offer a convenient way to calculate the cross product of two vectors, as discussed in Section A.5. The following recipe is used:

\[
a \times b = \begin{vmatrix} i & j & k \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} = \begin{vmatrix} a_y & a_z \\ b_y & b_z \end{vmatrix} - \begin{vmatrix} a_x & a_z \\ b_x & b_z \end{vmatrix} + \begin{vmatrix} a_x & a_y \\ b_x & b_y \end{vmatrix}
\]

\[
= (a_yb_z - a_zb_y)i + (a_zb_x - a_xb_z)j + (a_xb_y - a_yb_x)k
\]

Note that by referring to Property II, you can show that \( b \times a = -a \times b \).

### A.8 Working with Matrices

Physical chemists find widespread use for matrices. Matrices can be used to represent symmetry operations in the application of group theory to problems concerning molecular symmetry. They can also be used to obtain the energies of molecular orbitals formed through the linear combination of atomic orbitals. We next illustrate the use of matrices for representing the rotation operation that is frequently encountered in molecular symmetry considerations.

Consider the rotation of a three-dimensional vector about the \( z \) axis. Because the \( z \) component of the vector is unaffected by this operation, we need only consider the effect of the rotation operation on the two-dimensional vector formed by the projection of the three-dimensional vector on the \( x-y \) plane. The transformation can be represented by \((x_1, y_1, z_1) \rightarrow (x_2, y_2, z_2)\). The effect of the operation on the \( x \) and \( y \) components of the vector is shown in Figure A.14.

Next, relationships are derived among \((x_1, y_1, z_1), (x_2, y_2, z_2)\), the magnitude of the radius vector \( r \), and the angles \( \alpha \) and \( \beta \), based on the preceding figure. The magnitude of the radius vector \( r \) is

\[
r = \sqrt{x_1^2 + y_1^2 + z_1^2} = \sqrt{x_2^2 + y_2^2 + z_2^2}
\]
Although the values of $x$ and $y$ change in the rotation, $r$ is unaffected by this operation. The relationships between $x$, $y$, $r$, $\alpha$, and $\beta$ are given by

$$\theta = 180^\circ - \alpha - \beta$$

$$x_1 = r \cos \alpha, \quad y_1 = r \sin \alpha$$

$$x_2 = -r \cos \beta, \quad y_1 = r \sin \beta$$

In the following discussion, these identities are used:

$$\cos(\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$\sin(\alpha \pm \beta) = \sin \alpha \cos \beta \mp \cos \alpha \sin \beta$$

From Figure A.14, the following relationship between $x_2$ and $x_1$ and $y_1$ can be derived using the identities of Equation (A.75):

$$x_2 = -r \cos \beta = -r \cos(180^\circ - \alpha - \theta)$$

$$= r \sin 180^\circ \sin(-\theta - \alpha) - r \cos 180^\circ \cos(-\theta - \alpha)$$

$$= r \cos(-\theta - \alpha) = r \cos(\theta + \alpha) = r \cos \theta \cos \alpha - r \sin \theta \sin \alpha$$

$$= x_1 \cos \theta - y_1 \sin \theta$$

Using the same procedure, the following relationship between $y_2$ and $x_1$ and $y_1$ can be derived:

$$y_2 = x_1 \sin \theta + y_1 \cos \theta$$

Next, these results are combined to write the following equations relating $x_2$, $y_2$, and $z_2$ to $x_1$, $y_1$, and $z_1$:

$$x_2 = x_1 \cos \theta - y_1 \sin \theta$$

$$y_2 = x_1 \sin \theta + y_1 \cos \theta$$

$$z_2 = 0x_1 + 0y_1 + z_1$$

At this point, the concept of a matrix can be introduced. An $n \times m$ matrix is an array of numbers, functions, or operators that can undergo mathematical operations such as addition and multiplication with one another. The operation of interest to us in considering rotation about the $z$ axis is matrix multiplication. We illustrate how matrices, which are designated in bold script, such as $A$, are multiplied using $2 \times 2$ matrices as an example.

$$AB = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix}$$

Using numerical examples,

$$\begin{pmatrix} 2 & 1 \\ -3 & 4 \end{pmatrix} \begin{pmatrix} 1 & 6 \\ 2 & -1 \end{pmatrix} = \begin{pmatrix} 4 & 11 \\ 5 & -22 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 6 \\ 2 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \begin{pmatrix} -5 \\ 3 \end{pmatrix}$$

Now consider the initial and final coordinates $(x_1, y_1, z_1)$ and $(x_2, y_2, z_2)$ as $3 \times 1$ matrices $(x_1, y_1, z_1)$ and $(x_2, y_2, z_2)$. In that case, the set of simultaneous equations of Equation (A.78) can be written as

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$$

We see that we can represent the operator for rotation about the $z$ axis, $R_z$, as the following $3 \times 3$ matrix:

$$R_z = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
The rotation operator for $180^\circ$ and $120^\circ$ rotation can be obtained by evaluating the sine and cosine functions at the appropriate values of $\theta$. These rotation operators have the form

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

respectively (A.82)

One special matrix, the identity matrix designated $I$, deserves additional mention. The identity matrix corresponds to an operation in which nothing is changed. The matrix that corresponds to the transformation $(x_1, y_1, z_1) \rightarrow (x_2, y_2, z_2)$ expressed in equation form as

$$x_2 = x_1 + 0y_1 + 0z_1$$
$$y_2 = 0x_1 + y_1 + 0z_1$$
$$z_2 = 0x_1 + 0y_1 + z_1$$

is the identity matrix

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The identity matrix is an example of a diagonal matrix. It has this name because only the diagonal elements are nonzero. In the identity matrix of order $n \times n$, all diagonal elements have the value one.

The operation that results from the sequential operation of two individual operations represented by matrices $A$ and $B$ is the products of the matrices: $C = AB$. An interesting case illustrating this relationship is counterclockwise rotation through an angle $\theta$ followed by clockwise rotation through the same angle, which corresponds to rotation by $-\theta$. Because $\cos(-\theta) = \cos \theta$ and $\sin(-\theta) = -\sin \theta$, the rotation matrix for $-\theta$ must be

$$R_{-\theta} = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(A.84)

Because the sequential operations leave the vector unchanged, it must be the case that $R_x R_{-z} = R_{-z} R_x = I$. We verify here that the first of these relations is obeyed:

$$R_{-z} = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos^2 \theta + \sin^2 \theta & -\sin \theta \cos \theta + 0 & 0 \\ \sin \theta \cos \theta - \sin \theta \cos \theta + 0 & \cos^2 \theta + \sin^2 \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(A.85)

Any matrix $B$ that satisfies the relationship $AB = BA = I$ is called the inverse matrix of $A$ and is designated $A^{-1}$. Inverse matrices play an important role in finding the energies of a set of molecular orbitals that is a linear combination of atomic orbitals.