Chapter 17 – Determinants

Motivation: They are used to help construct wavefunctions which meet the requirements of asymmetry.

*17.1 Concepts

\[
\begin{vmatrix}
a_{11} & a_{12} & \cdots & a_{1n} \\
a_{21} & a_{22} & \cdots & a_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
a_{n1} & a_{n2} & \cdots & a_{nn}
\end{vmatrix} \rightarrow \det A = \begin{vmatrix}
a_{11} & a_{12} & \cdots & a_{1n} \\
a_{21} & a_{22} & \cdots & a_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
a_{n1} & a_{n2} & \cdots & a_{nn}
\end{vmatrix}
\]

- the idea of determinants come from solving simultaneous linear equations

- for a 2 x 2 matrix finding the \( \det A \) is fairly simple

\[
A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \rightarrow \det A = a_{11}a_{22} - a_{12}a_{21}
\]

- it gets more complicated for higher orders

*17.2 Determinants of Order 3

- Minors & Cofactors

-- the idea here is that we will be generating smaller 2 x 2 matrices from the original 3 x 3 one

-- defn: \( M_{ij} \) of element \( a_{ij} \) is given by creating a 2 x 2 matrix by eliminating the row and column the element appears in and using the remaining elements to generate a 2 x 2 determinant

\[
\begin{vmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{vmatrix} \rightarrow a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} + a_{12}a_{23}a_{31}
\]

\[
\begin{vmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{vmatrix} \rightarrow M_{11} = a_{22}a_{33} - a_{23}a_{32}
\]

\[
\begin{vmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{vmatrix} \rightarrow M_{12} = a_{11}a_{33} - a_{13}a_{31}
\]

\[
\begin{vmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{vmatrix} \rightarrow M_{13} = a_{11}a_{22} - a_{12}a_{21}
\]

-- the sign for the elements alternate which equates mathematically to \((-1)^{i+j}\)

\[
\begin{vmatrix}
+ & - & + \\
- & + & - \\
+ & - & +
\end{vmatrix}
\]

-- putting the minor together with the correct sign leads to the cofactor of the element: \( C_{ij} = (-1)^{i+j} M_{ij} \)

--- using the previous matrix say we want \( C_{23} \) and the \( C_{32} \)

\[
C_{23} : \begin{vmatrix} 1 & 2 & 3 \\ 1 & 4 & 9 \\ 1 & 5 & 7 \end{vmatrix} \rightarrow - \begin{vmatrix} 1 & 2 \\ 1 & 5 \end{vmatrix} = -(1\cdot 5 - 2\cdot 1) = -3
\]

\[
C_{32} : \begin{vmatrix} 1 & 2 & 3 \\ 1 & 4 & 9 \\ 1 & 5 & 7 \end{vmatrix} \rightarrow - \begin{vmatrix} 1 & 3 \\ 1 & 7 \end{vmatrix} = -(1\cdot 7 - 3\cdot 1) = -4
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\[
C_{32} : \begin{vmatrix} 1 & 2 & 3 \\ 1 & 4 & 9 \\ 1 & 5 & 7 \end{vmatrix} \rightarrow - \begin{vmatrix} 1 & 3 \\ 1 & 7 \end{vmatrix} = -(1\cdot 7 - 3\cdot 1) = -4
\]
*17.3 The General Case
- for an \( n \times n \) matrix the determinant is obtained by the expansion along any row or column:
  \[ D = \sum_{j=1}^{n} a_{ij} C_{ij} \text{ or } D = \sum_{i=1}^{n} a_{ij} C_{ij} \]
- example: Again back to our matrix let’s find the determinant both across a row and a column
  for the 3\(^{rd}\) row: \( i = 3 \) with
  \[ D = \sum_{j=1}^{3} a_{3j} C_{3j} \]
  \[ D = a_{31} C_{31} + a_{32} C_{32} + a_{33} C_{33} \]
  \[ D = 1 \epsilon (-1)^{3+1} \begin{vmatrix} 2 & 3 \\ 4 & 9 \end{vmatrix} + 5 \epsilon (-1)^{3+2} \begin{vmatrix} 1 & 3 \\ 1 & 9 \end{vmatrix} + 7 \epsilon (-1)^{3+3} \begin{vmatrix} 1 & 2 \\ 1 & 4 \end{vmatrix} \]
  \[ D = 1 \epsilon (2 \cdot 9 - 3 \cdot 4) + 5 \epsilon (-1)^{5} (1 \cdot 9 - 3 \cdot 1) + 7 \epsilon (-1)^{6} (1 \cdot 4 - 2 \cdot 1) \]
  \[ D = (18 - 12) - 5(9 - 3) + 7(4 - 2) \]
  \[ D = 6 - 30 + 14 = -10 \]
  For the 2\(^{nd}\) column: \( j = 2 \) with
  \[ D = \sum_{i=1}^{3} a_{i2} C_{i2} \]
  \[ D = a_{12} C_{12} + a_{22} C_{22} + a_{32} C_{32} \]
  \[ D = 2 \epsilon (-1)^{1+2} \begin{vmatrix} 1 & 9 \\ 1 & 7 \end{vmatrix} + 4 \epsilon (-1)^{2+2} \begin{vmatrix} 1 & 3 \\ 1 & 7 \end{vmatrix} + 5 \epsilon (-1)^{3+2} \begin{vmatrix} 1 & 3 \\ 1 & 9 \end{vmatrix} \]
  \[ D = -2 \epsilon (1 \cdot 7 - 9 \cdot 1) + 4 \epsilon (1 \cdot 7 - 3 \cdot 1) - 5 \epsilon (1 \cdot 9 - 3 \cdot 1) \]
  \[ D = 4 + 16 - 30 = -10 \]
  Therefore, it doesn’t matter how you get the determinant you will obtain the same answer through row or column expansion.

*17.4 The Solution of Linear Equations – Secular Equations
- this methodology is how we in fact solve eigenvalue problems
- wavefunctions may be represented as linear combinations of atomic orbitals (LCAOs) and so the Schrödinger equation may be solved using this technique
- we start as always with a set of equations:
  \[ a_{11} x_1 + a_{12} x_2 + \cdots + a_{1n} x_n = \lambda x_1 \]
  \[ \vdots \]
  \[ a_{n1} x_1 + a_{n2} x_2 + \cdots + a_{nn} x_n = \lambda x_n \]
- we then get all terms on one side of each equation or:
\[ a_1 x_1 - \lambda x_1 + a_{12} x_2 + \cdots + a_{1n} x_n = 0 \]
\[ \vdots \]
\[ a_{n1} x_1 - \lambda x_1 + a_{n2} x_2 + \cdots + a_{nn} x_n = 0 \]

which can be written as:
\[
\begin{bmatrix}
  a_{11} - \lambda & a_{12} & \cdots & a_{1n} \\
  a_{21} & a_{22} - \lambda & \cdots & a_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{n1} & a_{n2} & \cdots & a_{nn} - \lambda
\end{bmatrix}
\begin{bmatrix}
  x_1 \\
  x_2 \\
  \vdots \\
  x_n
\end{bmatrix}
= 0
\]

- the solutions of this equation is found through the determinant or

\[
\begin{vmatrix}
  a_{11} - \lambda & a_{12} & \cdots & a_{1n} \\
  a_{21} & a_{22} - \lambda & \cdots & a_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{n1} & a_{n2} & \cdots & a_{nn} - \lambda
\end{vmatrix} = 0
\]

- Example:
\[
\begin{align*}
3x + y + 0z &= -\lambda x \\
x + y + z &= 0 \\
0x + y + 3z &= 0
\end{align*}
\]

We will use cofactor expansion across the first row:
\[
(3-\lambda) \begin{vmatrix} 3-\lambda & 1 & 0 \\ 1 & 3-\lambda & 1 \\ 0 & 1 & 3-\lambda \end{vmatrix} = (3-\lambda)^3 - 1[(3-\lambda) - 0] + 0
\]
\[
= (3-\lambda)^3 - (3-\lambda) - 6\lambda + \lambda^2 - 9\lambda + 6\lambda^2 - \lambda^3 = 27 - 27\lambda + 9\lambda^2 - \lambda^3 = 0
\]

So, this turns into an equation where we are trying to locate the roots, 3, 3 ± \sqrt{2}

We then apply these roots into the equations:

for \( \lambda = 3 \):
\[
(3-3)x + y = 0 \rightarrow y = 0 \\
x + (3-3)0 + z = 0 \rightarrow x = -z
\]

for \( \lambda = 3 + \sqrt{2} \):
\[
(3-3-\sqrt{2})x + y = 0 \rightarrow \sqrt{2}x = y \\
x + (3-3-\sqrt{2})\sqrt{2}x + z = 0 \rightarrow x - 2x + z = 0 \rightarrow x = z
\]

for \( \lambda = 3 - \sqrt{2} \):
\[
(3-3+\sqrt{2})x + y = 0 \rightarrow -\sqrt{2}x = y \\
x + (3-3+\sqrt{2})(-\sqrt{2}x) + z = 0 \rightarrow x - 2x + z = 0 \rightarrow x = z
\]

*17.5 Properties of Determinants
- Transpose: \( \det A = \det A^T \)
- Multiplication by a constant:
\[
\begin{vmatrix}
\lambda a_1 & \lambda b_1 & \lambda c_1 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix} = \lambda \begin{vmatrix}
a_1 & b_1 & c_1 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix}
\]

- Zero row or column leads to a determinant which is zero
- Addition along any row or column is the sum of the two individual determinants
\[
\begin{vmatrix}
a_1 + d_1 & b_1 + d_2 & c_1 + d_3 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix} = \begin{vmatrix}
a_1 & b_1 & c_1 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix} + \begin{vmatrix}
d_1 & d_2 & d_3 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix}
\]

- Interchange of two rows or columns leads to a change in sign which is indicative of asymmetry and will be very important in quantum
\[
\begin{vmatrix}
a_1 & b_1 & c_1 \\
a_2 & b_2 & c_2 \\
a_3 & b_3 & c_3 \\
\end{vmatrix} = -\begin{vmatrix}
b_1 & a_1 & c_1 \\
b_2 & a_2 & c_2 \\
b_3 & a_3 & c_3 \\
\end{vmatrix} = -\begin{vmatrix}
a_3 & b_3 & c_3 \\
b_3 & a_3 & c_3 \\
a_1 & b_1 & c_1 \\
\end{vmatrix}
\]

- If two rows or columns have the same elements or are equal the determinant is zero

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*17.6 Reduction to triangular form – Skip

*17.7 Alternating Functions
- Matrices may be comprised of functions which is the case in many of our quantum descriptions
- Alternating functions are ones in which the exchange of two variables leads to a sign change in the original function: \( f(x_2, x_1, \ldots, x_n) = -f(x_1, x_2, \ldots, x_n) \)
- We will see this when we talk about spin orbitals and the Slater determinant