

## MATRICES CHEMISTRY 273

Instead of a lecture (to a sleeping audience!) on matrix operations, I would like you to study this handout. It includes material relevant to our work in quantum mechanics and group theory. If you already know how to handle matrices, check the sample problems to be sure. If you don't, use this sheet, the material in standard texts (e.g., Lowe, pp. 267-275, 485-487; D. T. Finkbeiner, *Introduction to Matrices and Linear Transformations*, etc.) and the instructor to become fluent with the following concepts. For formal derivations and simple numerical examples used in class, it is important to be able to do the following exercises "by hand." For anything more complicated on homework, exams, or research you will have MATLAB or MATHEMATICA available and should know how to use them.

Instructions for using MATLAB, Mathematica, and GAUSSIAN on the chemistry compuserver can be found at <http://www.chemistry.ucsc.edu/teaching/switkes/CHEM273/computing.html> (you must have a departmental account to run these programs).

- I. Definition. The  $m \times n$  matrix  $\underline{\underline{A}}$  is a rectangular array of  $m \ n$  numbers ( $m$  rows,  $n$  columns):

$$\begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & & & \vdots \\ a_{m1} & \dots & \dots & a_{mn} \end{pmatrix}$$

- II. Matrix multiplication: The product  $\underline{\underline{A}} \underline{\underline{B}} = \underline{\underline{C}}$  is defined as:

$$(\underline{\underline{AB}})_{ij} = c_{ij} = \sum_k a_{ik} b_{kj}$$

Example:

$$\underline{\underline{A}} = \begin{pmatrix} 1 & 6 & 2 \\ 3 & 5 & 9 \\ 7 & 1 & 3 \end{pmatrix} \quad \underline{\underline{B}} = \begin{pmatrix} 8 & 6 & 2 \\ 1 & 5 & 1 \\ 3 & 7 & 4 \end{pmatrix}$$

$$\underline{\underline{A}} \underline{\underline{B}} = \underline{\underline{C}} \quad \begin{aligned} c_{11} &= 1 \cdot 8 + 6 \cdot 1 + 2 \cdot 3 = 20 \\ c_{21} &= 3 \cdot 8 + 5 \cdot 1 + 9 \cdot 3 = 56 \\ c_{12} &= 1 \cdot 6 + 6 \cdot 5 + 2 \cdot 7 = 50 \end{aligned}$$

**Problem:** Show that

$$\underline{\underline{A}} \underline{\underline{B}} = \begin{pmatrix} 20 & 50 & 16 \\ 56 & 106 & 47 \\ 66 & 68 & 27 \end{pmatrix}$$

**Problem:** Let

$$\underline{\underline{D}} = \begin{pmatrix} 3 \\ 5 \\ 2 \end{pmatrix}. \text{ Show that: } \underline{\underline{A}} \underline{\underline{D}} = \begin{pmatrix} 37 \\ 52 \\ 32 \end{pmatrix}.$$

Does it make sense to talk about the matrix product  $\underline{\underline{D}} \underline{\underline{A}}$ ?

CHEMISTRY 273

III. Matrices do not necessarily commute, i.e., in general  $\underline{\underline{A}} \underline{\underline{B}} \neq \underline{\underline{B}} \underline{\underline{A}}$ .

**Problem:** Show that  $\underline{\underline{A}}$  and  $\underline{\underline{B}}$  in II do not commute.

IV. Definition. The unit matrix:

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

V. Definition: The inverse of a matrix  $\underline{\underline{F}}$  is the matrix  $\underline{\underline{F}}^{-1}$  with the properties  $\underline{\underline{F}} \underline{\underline{F}}^{-1} = \underline{\underline{F}}^{-1} \underline{\underline{F}} = \underline{\underline{I}}$ .

**Problem:** Show that if

$$\underline{\underline{F}} = \begin{pmatrix} 3 & 1 \\ 2 & 4 \end{pmatrix} \quad \text{then} \quad \underline{\underline{F}}^{-1} = \begin{pmatrix} .4 & -.1 \\ -.2 & .3 \end{pmatrix}.$$

VI. Definition: The transpose of a matrix  $\underline{\underline{A}}$  is the matrix  $\underline{\underline{\tilde{A}}}$  where  $(\underline{\underline{\tilde{A}}})_{ij} = a_{ji}$ .

VII. Definition: A unitary matrix  $\underline{\underline{U}}$  is one where  $\underline{\underline{\tilde{U}}}^* = \underline{\underline{U}}^{-1}$ .

An orthogonal matrix  $\underline{\underline{U}}$  is one where  $\underline{\underline{\tilde{U}}} = \underline{\underline{U}}^{-1}$ .

**Problem:** Show that

$$\underline{\underline{U}} = \begin{pmatrix} \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \end{pmatrix} \text{ is unitary.}$$

VIII. Definition: The trace of a matrix  $\underline{\underline{A}}$  is:

$$\text{tr} \underline{\underline{A}} = \sum_i a_{ii}$$

**Problem:** Prove in general that  $\text{tr}(\underline{\underline{\tilde{U}}}^* \underline{\underline{A}} \underline{\underline{U}}) = \text{tr}(\underline{\underline{A}})$  where  $\underline{\underline{U}}$  is a unitary matrix.

Or: show that  $\text{tr}(\underline{\underline{\tilde{U}}}^* \underline{\underline{F}} \underline{\underline{U}}) = \text{tr}(\underline{\underline{F}})$  where  $\underline{\underline{F}}$  is given in Section V and  $\underline{\underline{U}}$  in Section VII above.

Note: These are examples of the more general  $\text{tr}(\underline{\underline{B}}^{-1} \underline{\underline{A}} \underline{\underline{B}}) = \text{tr}(\underline{\underline{A}})$ .

CHEMISTRY 273

IX. Definitions: A symmetric matrix,  $\underline{\underline{S}}$ , is one where  $\underline{\underline{S}} = \underline{\underline{S}}^T$ .

A hermitian matrix is one where  $\underline{\underline{H}} = (\underline{\underline{H}})^*$ . Here  $(\underline{\underline{H}})^*_{ij} = \underline{\underline{H}}^*_{ji}$ . For matrices containing only real numbers, the terms hermitian and symmetric are equivalent.

X. Definitions: A diagonal matrix  $\underline{\underline{E}}$  has the form:

$$\underline{\underline{E}} = \begin{pmatrix} \epsilon_1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & \epsilon_2 & 0 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \epsilon_n \end{pmatrix}$$

XI. Fact: For every hermitian matrix there exists a unitary matrix which diagonalizes it:

$$\underline{\underline{U}}^* \underline{\underline{H}} \underline{\underline{U}} = \underline{\underline{E}}. \text{ The numbers } \epsilon_1, \epsilon_2 \dots \epsilon_n \text{ are the eigenvalues of the matrix } \underline{\underline{H}}.$$

**Problem:** Given

$$\underline{\underline{H}} = \begin{pmatrix} 3 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix}$$

Show that  $\underline{\underline{U}}$  given in VII diagonalizes  $\underline{\underline{H}}$ . What are the eigenvalues of  $\underline{\underline{H}}$ ?

**Problem:** Given

$$\underline{\underline{H}}' = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix} \quad \text{and} \quad \underline{\underline{U}}' = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

Show that  $\underline{\underline{U}}'$  diagonalizes  $\underline{\underline{H}}'$ . What are the eigenvalues of  $\underline{\underline{H}}'$ ?  $\underline{\underline{H}}'$  and  $\underline{\underline{U}}'$  are related to the molecular orbital description of the homonuclear diatomic. What is this relationship?

XII. To find the eigenvalues and unitary transformation which diagonalizes a matrix:

a.  $\underline{\underline{U}}^* \underline{\underline{H}} \underline{\underline{U}} = \underline{\underline{E}}$

$$\underline{\underline{H}} \underline{\underline{U}} = \underline{\underline{U}} \underline{\underline{E}}$$

b. Break  $\underline{\underline{U}}$  into the column vectors  $\underline{\underline{L}}_i$ . For each of the column vectors show that:

$$\underline{\underline{H}} (\underline{\underline{L}})_i = (\underline{\underline{L}})_i \epsilon_i = \epsilon_i (\underline{\underline{L}})_i$$

$$\text{thus } (\underline{\underline{H}} - \epsilon_i \underline{\underline{I}}) (\underline{\underline{L}})_i = 0.$$

CHEMISTRY 273

The above (for each  $i$ ) is a set of homogeneous linear equations which will only have non-trivial solutions (non-zero values for  $\underline{L}_i$ ) if the determinant of the coefficients  $|\underline{H} - \epsilon \underline{1}| = 0$ . For a given  $\underline{H}$  the only possible values of  $\epsilon$  which give a zero determinant are the eigenvalues of  $\underline{H}$  (the diagonal elements of  $\underline{E}$ ). If any of these possible  $\epsilon$ 's are substituted into  $\underline{H} \underline{L}_i = \underline{L}_i \epsilon_i$ , the column vector  $\underline{L}_i$  corresponding to the eigenvalue  $\epsilon_i$  may be found (one must also use the relation  $\sum_i U_{ij}^2 = 1$  which comes from the unitary nature of  $\underline{U}$ ).  $\underline{L}_i$  is the *eigenvector* for *eigenvalue*  $\epsilon_i$ .

Example: Find the eigenvalues and eigenvectors of  $\underline{H}'$  above:

$$\begin{vmatrix} (2-\epsilon) & 1 \\ 1 & (2-\epsilon) \end{vmatrix} = 0 \quad \begin{aligned} &= (2-\epsilon)^2 - 1^2 \\ &= \epsilon^2 - 4\epsilon + 3 = 0 \end{aligned}$$

$$\epsilon = \frac{4 \pm \sqrt{4}}{2} = 3 \text{ or } 1 \quad \text{so} \quad \underline{E} = \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}$$

for  $\epsilon_1 = 3$

$$(\underline{H} - \epsilon_1 \underline{1}) \underline{L}_1 = \underline{0}$$

$$\begin{pmatrix} 2-3 & 1 \\ 1 & 2-3 \end{pmatrix} \begin{pmatrix} U_{11} \\ U_{21} \end{pmatrix} = 0$$

$$\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} U_{11} \\ U_{22} \end{pmatrix} = 0$$

$$-U_{11} + U_{21} = 0$$

$$U_{11} - U_{21} = 0$$

$$U_{11} = U_{21}$$

$$\text{also } U_{11}^2 + U_{21}^2 = 1$$

$$\text{so } U_{11} = U_{21} = \frac{1}{\sqrt{2}}$$

$$\text{and } \underline{L}_1 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

for  $\epsilon_2 = 1$

$$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} U_{12} \\ U_{22} \end{pmatrix} = 0$$

$$U_{12} + U_{22} = 0$$

$$U_{12} = -U_{22}$$

$$U_{12}^2 + U_{22}^2 = 1$$

$$U_{12} = \sqrt{\frac{1}{2}} \quad U_{22} = -\sqrt{\frac{1}{2}}$$

$$\underline{U}_2 = \begin{pmatrix} \sqrt{\frac{1}{2}} \\ -\sqrt{\frac{1}{2}} \end{pmatrix}$$

thus

$$\underline{U} = \begin{pmatrix} \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \end{pmatrix} \quad \underline{E} = \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}$$

**Problem:** Derive the eigenvalues and unitary transformation which diagonalizes

$$\underline{H} = \begin{pmatrix} 3 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix}$$