

Modern Quantum Chemistry, Szabo & Ostlund

HW

王石嵘

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1 Mathematical Review

1.1 Linear Algebra

1.1.1 3-D Vector Algebra

Ex 1.1

a)

$$\mathcal{O}\mathbf{e}_j = \sum_{i=1}^3 \mathbf{e}_i O_{ij} \quad (1.1.1)$$

$$\mathbf{e}_i \cdot \mathcal{O}\mathbf{e}_j = \mathbf{e}_i \cdot \sum_{i=1}^3 \mathbf{e}_i O_{ij} = O_{ij} \quad (1.1.2)$$

b)

$$\begin{aligned} \mathbf{b} = \mathcal{O}\mathbf{a} &= \sum_{i=1}^3 a_i \sum_{j=1}^3 \mathbf{e}_j O_{ji} \\ &= \sum_{j=1}^3 a_j \sum_{i=1}^3 \mathbf{e}_i O_{ij} = \sum_{i=1}^3 \mathbf{e}_i \sum_{j=1}^3 a_j O_{ij} \end{aligned} \quad (1.1.3)$$

thus

$$\mathbf{b}_i = \sum_{j=1}^3 a_j O_{ij} \quad (1.1.4)$$

Ex 1.2

$$[\mathbf{A}, \mathbf{B}] = \begin{bmatrix} 0 & -2 & 4 \\ 2 & 0 & 3 \\ -4 & -3 & 0 \end{bmatrix} \quad (1.1.5)$$

$$\{\mathbf{A}, \mathbf{B}\} = \begin{bmatrix} 0 & 0 & -2 \\ 0 & -2 & 3 \\ -2 & 3 & -2 \end{bmatrix} \quad (1.1.6)$$

1.1.2 Matrices

Ex 1.3

$$(AB)_{nk} = \sum_m^M A_{nm} B_{mk} \quad (1.1.7)$$

$$(AB)_{kn}^\dagger = (AB)_{nk}^* = \sum_m^M A_{nm}^* B_{mk}^* = \sum_m^M B_{km}^\dagger A_{mn}^\dagger = (B^\dagger A^\dagger)_{kn} \quad (1.1.8)$$

thus

$$(\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger \quad (1.1.9)$$

Ex 1.4

a. suppose \mathbf{A} is $N \times M$ and \mathbf{B} is $M \times N$

$$\text{tr } \mathbf{AB} = \sum_n^N (AB)_{nn} = \sum_n^N \sum_m^M A_{nm} B_{mn} = \sum_m^M \sum_n^N B_{mn} A_{nm} = \sum_m^M (BA)_{mm} = \text{tr } \mathbf{BA} \quad (1.1.10)$$

b.

$$\mathbf{AB}(\mathbf{AB})^{-1} = \mathbf{1} \quad (1.1.11)$$

$$\mathbf{B}^{-1}\mathbf{A}^{-1}\mathbf{AB}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1}\mathbf{1} \quad (1.1.12)$$

$$\mathbf{B}^{-1}(\mathbf{A}^{-1}\mathbf{A})\mathbf{B}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \quad (1.1.13)$$

$$\mathbf{B}^{-1}\mathbf{1B}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \quad (1.1.14)$$

thus

$$(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \quad (1.1.15)$$

c.

$$\mathbf{B} = \mathbf{U}^\dagger \mathbf{A} \mathbf{U} \quad (1.1.16)$$

huhhj

$$\mathbf{UBU}^\dagger = \mathbf{UU}^\dagger \mathbf{A} \mathbf{UU}^\dagger = \mathbf{1A1} = \mathbf{A} \quad (1.1.17)$$

d. $\because \mathbf{C}$ is Hermitian, \therefore

$$\mathbf{C} = \mathbf{C}^\dagger \quad (1.1.18)$$

$$\mathbf{AB} = (\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger \quad (1.1.19)$$

Since \mathbf{A}, \mathbf{B} are Hermitian,

$$\mathbf{AB} = \mathbf{B}^\dagger \mathbf{A}^\dagger = \mathbf{BA} \quad (1.1.20)$$

\therefore

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} = 0 \quad (1.1.21)$$

i.e. \mathbf{A}, \mathbf{B} commute

e. Since \mathbf{A} is Hermitian,

$$\mathbf{A} = \mathbf{A}^\dagger \quad (1.1.22)$$

thus

$$(\mathbf{A}^{-1})^\dagger \mathbf{A} = (\mathbf{A}^{-1})^\dagger \mathbf{A}^\dagger = (\mathbf{A} \mathbf{A}^{-1})^\dagger = \mathbf{1}^\dagger = \mathbf{1} \quad (1.1.23)$$

thus

$$(\mathbf{A}^{-1})^\dagger \mathbf{A} \mathbf{A}^{-1} = \mathbf{A}^{-1} \quad (1.1.24)$$

$$(\mathbf{A}^{-1})^\dagger = \mathbf{A}^{-1} \quad (1.1.25)$$

i.e. \mathbf{A}^{-1} , if it exists, is Hermitian.

f. Suppose

$$\mathbf{A}^{-1} = \begin{pmatrix} x & y \\ z & w \end{pmatrix} \quad (1.1.26)$$

thus

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} x & y \\ z & w \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (1.1.27)$$

the solution is

$$\begin{aligned} x &= \frac{A_{22}}{A_{11}A_{22} - A_{12}A_{21}} \\ y &= \frac{-A_{12}}{A_{11}A_{22} - A_{12}A_{21}} \\ z &= \frac{-A_{21}}{A_{11}A_{22} - A_{12}A_{21}} \\ w &= \frac{A_{11}}{A_{11}A_{22} - A_{12}A_{21}} \end{aligned} \quad (1.1.28)$$

thus

$$\mathbf{A}^{-1} = \frac{1}{\det(\mathbf{A})} \begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix} \quad (1.1.29)$$

1.1.3 Determinants

Ex 1.5 Suppose

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \quad (1.1.30)$$

1.

$$\begin{vmatrix} 0 & 0 \\ A_{21} & A_{22} \end{vmatrix} = 0 \cdot A_{22} - 0 \cdot A_{21} = 0 \quad (1.1.31)$$

$$\begin{vmatrix} 0 & A_{12} \\ 0 & A_{22} \end{vmatrix} = 0 \cdot A_{22} - 0 \cdot A_{12} = 0 \quad (1.1.32)$$

2.

$$\det(\mathbf{A}) = A_{11}A_{22} - 0 \cdot 0 = A_{11}A_{22} \quad (1.1.33)$$

3.

$$\det(\mathbf{A}) = A_{11}A_{22} - A_{12}A_{21} \quad (1.1.34)$$

$$\begin{vmatrix} A_{21} & A_{22} \\ A_{11} & A_{12} \end{vmatrix} = A_{21}A_{12} - A_{22}A_{11} = -\det(\mathbf{A}) \quad (1.1.35)$$

4.

$$\det(\mathbf{A}^\dagger)^* = \begin{vmatrix} A_{11}^* & A_{21}^* \\ A_{12}^* & A_{22}^* \end{vmatrix}^* = (A_{11}^*A_{22}^* - A_{21}^*A_{12}^*)^* = A_{11}A_{22} - A_{12}A_{21} = \det(\mathbf{A}) \quad (1.1.36)$$

5. Suppose $\mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$

$$\begin{aligned} \det(\mathbf{AB}) &= \begin{vmatrix} A_{11}B_{11} + A_{12}B_{21} & A_{11}B_{12} + A_{12}B_{22} \\ A_{21}B_{11} + A_{22}B_{21} & A_{21}B_{12} + A_{22}B_{22} \end{vmatrix} \\ &= (A_{11}B_{11} + A_{12}B_{21})(A_{21}B_{12} + A_{22}B_{22}) - (A_{11}B_{12} + A_{12}B_{22})(A_{21}B_{11} + A_{22}B_{21}) \\ &= A_{11}B_{11}A_{21}B_{12} + A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} + A_{12}B_{21}A_{22}B_{22} \\ &\quad - (A_{11}B_{12}A_{21}B_{11} + A_{11}B_{12}A_{22}B_{21} + A_{12}B_{22}A_{21}B_{11} + A_{12}B_{22}A_{22}B_{21}) \\ &= A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} - A_{11}B_{12}A_{22}B_{21} - A_{12}B_{22}A_{21}B_{11} \end{aligned} \quad (1.1.37)$$

$$\begin{aligned} \det(\mathbf{A})\det(\mathbf{B}) &= (A_{11}A_{22} - A_{12}A_{21})(B_{11}B_{22} - B_{12}B_{21}) \\ &= A_{11}A_{22}B_{11}B_{22} - A_{11}A_{22}B_{12}B_{21} - A_{12}A_{21}B_{11}B_{22} + A_{12}A_{21}B_{12}B_{21} \\ &= A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} - A_{11}B_{12}A_{22}B_{21} - A_{12}B_{22}A_{21}B_{11} \end{aligned} \quad (1.1.38)$$

\therefore

$$\det(\mathbf{A})\det(\mathbf{B}) = \det(\mathbf{AB}) \quad (1.1.39)$$

Ex 1.6

6. If two rows (e.g. i th and j th) are equal

$$\det(\mathbf{A}) = \begin{vmatrix} \dots & \dots & \dots & \dots \\ A_{i1} & A_{i2} & \dots & A_{in} \\ \dots & \dots & \dots & \dots \\ A_{j1} & A_{j2} & \dots & A_{jn} \\ \dots & \dots & \dots & \dots \end{vmatrix} \xrightarrow{1.5.3} - \begin{vmatrix} \dots & \dots & \dots & \dots \\ A_{j1} & A_{j2} & \dots & A_{jn} \\ \dots & \dots & \dots & \dots \\ A_{i1} & A_{i2} & \dots & A_{in} \\ \dots & \dots & \dots & \dots \end{vmatrix} = - \begin{vmatrix} \dots & \dots & \dots & \dots \\ A_{i1} & A_{i2} & \dots & A_{in} \\ \dots & \dots & \dots & \dots \\ A_{j1} & A_{j2} & \dots & A_{jn} \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (1.1.40)$$

i.e.

$$\det(\mathbf{A}) = -\det(\mathbf{A}) \quad (1.1.41)$$

thus

$$\det(\mathbf{A}) = 0 \quad (1.1.42)$$

7. From Ex 1.5.5, we have

$$\det(\mathbf{A}) \det(\mathbf{A}^{-1}) = \det(\mathbf{1}) = 1 \quad (1.1.43)$$

thus

$$\det(\mathbf{A}^{-1}) = \det(\mathbf{A})^{-1} \quad (1.1.44)$$

8.

$$\mathbf{A}\mathbf{A}^\dagger = \mathbf{1} \Rightarrow \det(\mathbf{A}) \det(\mathbf{A}^\dagger) = \det(\mathbf{1}) = 1 \quad (1.1.45)$$

From Ex 1.5.4, we have

$$\det(\mathbf{A}) \det(\mathbf{A})^* = 1 \quad (1.1.46)$$

9. From Ex 1.5.5, we get

$$\det(\mathbf{U}^\dagger) \det(\mathbf{O}) \det(\mathbf{U}) = \det(\mathbf{O}) \quad (1.1.47)$$

and

$$\det(\mathbf{U}^\dagger) \det(\mathbf{U}) = \det(\mathbf{1}) = 1 \quad (1.1.48)$$

\therefore

$$\det(\mathbf{O}) = \det(\mathbf{O}) \quad (1.1.49)$$

Ex 1.7 If $\det(\mathbf{A}) \neq 0$, thus \mathbf{A}^{-1} exists, we have

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{c} = \mathbf{0} \Rightarrow \mathbf{c} = \mathbf{0} \quad (1.1.50)$$

□

1.1.4 N-D Complex Vector Spaces

1.1.5 Change of Basis

Ex 1.8

$$\Omega_{\alpha\beta} = \sum_{ij} U_{\alpha i}^\dagger O_{ij} U_{j\beta} \quad (1.1.51)$$

gives

$$\begin{aligned} \text{tr } \Omega &= \sum_{\alpha} \Omega_{\alpha\alpha} = \sum_{\alpha} \sum_{ij} U_{\alpha i}^\dagger O_{ij} U_{j\alpha} \\ &= \sum_{ij} O_{ij} \sum_{\alpha} U_{j\alpha} U_{\alpha i}^\dagger = \sum_{ij} O_{ij} \delta_{ji} = \text{tr } \mathbf{O} \end{aligned} \quad (1.1.52)$$

1.1.6 The Eigenvalue Problem

Ex 1.9

$$\mathbf{O}\mathbf{U} = \mathbf{U}\boldsymbol{\omega} \Rightarrow \mathbf{O}(\mathbf{c}^1 \quad \mathbf{c}^2 \quad \cdots \quad \mathbf{c}^N) = (\omega_1 \mathbf{c}_1 \quad \omega_2 \mathbf{c}_2 \quad \cdots \quad \omega_N \mathbf{c}_N) \quad (1.1.53)$$

thus

$$\mathbf{O}\mathbf{c}^\alpha = \omega_\alpha \mathbf{c}^\alpha \quad (1.1.54)$$

Ex 1.10

$$\begin{cases} O_{11} - \omega + O_{12}c = 0 \\ O_{21} + (O_{22} - \omega)c = 0 \end{cases} \quad (1.1.55)$$

$$(O_{11} - \omega)(O_{22} - \omega) - O_{21}O_{12} = 0 \quad (1.1.56)$$

$$\omega^2 - (O_{11} + O_{22})\omega + O_{11}O_{22} - O_{21}O_{12} = 0 \quad (1.1.57)$$

$$\begin{cases} \omega_1 = \frac{1}{2} \left(O_{11} + O_{22} - \sqrt{(O_{11} - O_{22})^2 + 4O_{21}O_{12}} \right) \\ \omega_2 = \frac{1}{2} \left(O_{11} + O_{22} + \sqrt{(O_{11} - O_{22})^2 + 4O_{21}O_{12}} \right) \end{cases} \quad (1.1.58)$$

Ex 1.11

a)

$$\begin{vmatrix} 3-\omega & 1 \\ 1 & 3-\omega \end{vmatrix} = 0 \Rightarrow (3-\omega)^2 - 1 = 0 \quad (1.1.59)$$

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \quad (1.1.60)$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (1.1.61)$$

$$\begin{vmatrix} 3-\omega & 1 \\ 1 & 2-\omega \end{vmatrix} = 0 \Rightarrow (3-\omega)(2-\omega) - 1 = 0 \quad (1.1.62)$$

Eigenvalues

$$\omega_1 = \frac{5+\sqrt{5}}{2} \quad \omega_2 = \frac{5-\sqrt{5}}{2} \quad (1.1.63)$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \frac{1}{2}(1+\sqrt{5}) \\ 1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} \frac{1}{2}(1-\sqrt{5}) \\ 1 \end{pmatrix} \quad (1.1.64)$$

b)

$$\theta_0 = \frac{1}{2} \tan^{-1} \frac{2O_{12}}{O_{11} - O_{12}} \quad (1.1.65)$$

for **A**

$$\theta_0 = \frac{1}{2} \tan^{-1} \frac{2 \times 1}{3-3} = \frac{\pi}{4} \quad (1.1.66)$$

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \quad (1.1.67)$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \sqrt{2}/2 \\ -\sqrt{2}/2 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} \sqrt{2}/2 \\ \sqrt{2}/2 \end{pmatrix} \quad (1.1.68)$$

for **B**

$$\theta_0 = \frac{1}{2} \tan^{-1} \frac{2 \times 1}{3-2} = \frac{1}{2} \tan^{-1} 2 \quad (1.1.69)$$

Eigenvalues

$$\omega_1 = \frac{10}{5+\sqrt{5}} = \frac{5-\sqrt{5}}{2} \quad \omega_2 = \frac{10}{5-\sqrt{5}} = \frac{5+\sqrt{5}}{2} \quad (1.1.70)$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \sqrt{\frac{\sqrt{5}+5}{10}} \\ \sqrt{\frac{2}{\sqrt{5}+5}} \end{pmatrix} = \sqrt{\frac{2}{\sqrt{5}+5}} \begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ 1 \end{pmatrix} \quad (1.1.71)$$

$$\mathbf{c}^2 = \begin{pmatrix} \sqrt{\frac{2}{\sqrt{5}+5}} \\ -\sqrt{\frac{\sqrt{5}+5}{10}} \end{pmatrix} = -\sqrt{\frac{\sqrt{5}+5}{10}} \begin{pmatrix} \frac{1-\sqrt{5}}{2} \\ 1 \end{pmatrix} \quad (1.1.72)$$

Details are in `chap1-1.nb`

1.1.7 Functions of Matrices

Ex 1.12

a.

$$\mathbf{A}^n = \mathbf{U} \mathbf{a}^n \mathbf{U}^\dagger \quad (1.1.73)$$

$$\det(\mathbf{A}^n) = \det(\mathbf{U}) \det(\mathbf{a}^n) \det(\mathbf{U}^\dagger) = \det(\mathbf{U}) \det(\mathbf{U}^\dagger) \begin{vmatrix} a_1^n & & & \\ & a_2^n & & \\ & & \ddots & \\ & & & a_N^n \end{vmatrix} = a_1^n a_2^n \cdots a_N^n \quad (1.1.74)$$

b. From 1.4.a, we have

$$\text{tr } \mathbf{A}^n = \text{tr}(\mathbf{U} \mathbf{a}^n \mathbf{U}^\dagger) = \text{tr}(\mathbf{U} \mathbf{U}^\dagger \mathbf{a}^n) = \text{tr}(\mathbf{a}^n) = \sum_{\alpha=1}^N a_\alpha^n \quad (1.1.75)$$

c.

$$\mathbf{U}^\dagger (\omega \mathbf{1} - \mathbf{A}) \mathbf{U} = \omega \mathbf{1} - \mathbf{a} \quad (1.1.76)$$

$$(\omega \mathbf{1} - \mathbf{A})^{-1} = [(\mathbf{U}(\omega \mathbf{1} - \mathbf{a})\mathbf{U}^\dagger)]^{-1} = \mathbf{U}(\omega \mathbf{1} - \mathbf{a})^{-1} \mathbf{U}^\dagger \quad (1.1.77)$$

while

$$(\omega \mathbf{1} - \mathbf{a})^{-1} = \begin{pmatrix} \omega - a_1 & & & \\ & \omega - a_2 & & \\ & & \ddots & \\ & & & \omega - a_N \end{pmatrix}^{-1} = \begin{pmatrix} \frac{1}{\omega - a_1} & & & \\ & \frac{1}{\omega - a_2} & & \\ & & \ddots & \\ & & & \frac{1}{\omega - a_N} \end{pmatrix} \quad (1.1.78)$$

thus

$$\mathbf{G}(\omega) = (\omega \mathbf{1} - \mathbf{A})^{-1} = \mathbf{U} \begin{pmatrix} \frac{1}{\omega - a_1} & & & \\ & \frac{1}{\omega - a_2} & & \\ & & \ddots & \\ & & & \frac{1}{\omega - a_N} \end{pmatrix} \mathbf{U}^\dagger \quad (1.1.79)$$

$$\mathbf{G}(\omega)_{ij} = \sum_{\alpha} U_{i\alpha} \frac{1}{\omega - a_{\alpha}} U_{\alpha j}^\dagger = \sum_{\alpha} \frac{U_{i\alpha} U_{j\alpha}^*}{\omega - a_{\alpha}} \quad (1.1.80)$$

Since $U_{i\alpha} = \langle i | \alpha \rangle$, $U_{\alpha j}^\dagger = U_{j\alpha}^* = \langle \alpha | j \rangle$

$$\mathbf{G}(\omega)_{ij} = \sum_{\alpha} \frac{\langle i | \alpha \rangle \langle \alpha | j \rangle}{\omega - a_{\alpha}} \quad (1.1.81)$$

Ex 1.13 The eigenvalues and eigenvectors of \mathbf{A} are

$$\omega_1 = a - b \quad \omega_2 = a + b \quad (1.1.82)$$

$$\mathbf{c}^1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (1.1.83)$$

$$\mathbf{A} = \mathbf{U} \mathbf{a} \mathbf{U}^\dagger = \frac{\sqrt{2}}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} a+b & 0 \\ 0 & a-b \end{pmatrix} \frac{\sqrt{2}}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad (1.1.84)$$

$$\begin{aligned} f(\mathbf{A}) &= \mathbf{U} f(\mathbf{a}) \mathbf{U}^\dagger = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} f(a+b) & 0 \\ 0 & f(a-b) \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} f(a+b) & f(a-b) \\ f(a+b) & -f(a-b) \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} f(a+b) + f(a-b) & f(a+b) - f(a-b) \\ f(a+b) - f(a-b) & f(a+b) + f(a-b) \end{pmatrix} \end{aligned} \quad (1.1.85)$$

1.2 Orthogonal Functions, Eigenfunctions, and Operators

Ex 1.14

$$\int_{-\infty}^{\infty} dx a(x) \delta(x) = \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{\varepsilon} dx a(x) \frac{1}{2\varepsilon} = \lim_{\varepsilon \rightarrow 0} \frac{1}{2\varepsilon} \int_{-\varepsilon}^{\varepsilon} dx a(x) \stackrel{\text{L'Hôpital}}{=} \lim_{\varepsilon \rightarrow 0} \frac{a(\varepsilon) - [-a(-\varepsilon)]}{2} = a(0) \quad (1.2.1)$$

1.2.1