Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

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Contents

1 Mathematical Review

1.1 Linear Algebra

1.1.1 3-D Vector Algebra

Ex 1.1

a)

$$\mathscr{O}\mathbf{e}_j = \sum_{i=1}^{3} \mathbf{e}_i O_{ij} \tag{1.1.1}$$

$$\mathbf{e}_i \cdot \mathscr{O}\mathbf{e}_j = \mathbf{e}_i \cdot \sum_{i=1}^{3} \mathbf{e}_i O_{ij} = O_{ij} \tag{1.1.2}$$

b)

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

thus

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

Ex 1.2

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

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

1.1.2 Matrices

Ex 1.3

$$(AB)_{nk} = \sum_{m}^{M} A_{nm} B_{mk} \tag{1.1.7}$$

$$(AB)^\dagger_{kn} = (AB)^*_{nk} = \sum_{m}^{M} A^*_{nm} B^*_{mk} = \sum_{m}^{M} B^\dagger_{km} A^\dagger_{mn} = (B^\dagger A^\dagger)_{kn} \tag{1.1.8}$$

thus

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

Ex 1.4

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

$$\operatorname{tr} \mathbf{AB} = \sum_{n}^{N} (AB)_{nn} = \sum_{n}^{N} \sum_{m}^{M} A_{nm} B_{mn} = \sum_{m}^{M} \sum_{n}^{N} B_{mn} A_{nm} = \sum_{m}^{M} (BA)_{mm} = \operatorname{tr} \mathbf{BA} \tag{1.1.10}$$

b.

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

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

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

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

thus

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

c.

$$\mathbf{B} = \mathbf{U}^{\dagger}\mathbf{AU} \tag{1.1.16}$$

huhhj

$$\mathbf{UBU}^{\dagger} = \mathbf{UU}^{\dagger}\mathbf{AUU}^{\dagger} = \mathbf{1A1} = \mathbf{A} \tag{1.1.17}$$

d. $\because$ **C** is Hermitian, $\therefore$

$$\mathbf{C} = \mathbf{C}^{\dagger} \tag{1.1.18}$$

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

Since **A**, **B** are Hermitian,

$$\mathbf{AB} = \mathbf{B}^{\dagger}\mathbf{A}^{\dagger} = \mathbf{BA} \tag{1.1.20}$$

$\therefore$

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

i.e. **A**, **B** commute

e. Since **A** is Hermitian,

$$\mathbf{A} = \mathbf{A}^{\dagger} \tag{1.1.22}$$

thus

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

thus

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

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

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

f. Suppose

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

thus

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

the solution is

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

thus

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

1.1.3 Determinants

Ex 1.5 Suppose

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

1.

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

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

2.

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

3.

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

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

4.

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

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

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

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

$\therefore$

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

Ex 1.6

6. If two rows (e.g. ith and jth) are equal

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

i.e.

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

thus

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

7. From Ex 1.5.5, we have

$$\det(\mathbf{A})\det\left(\mathbf{A}^{-1}\right) = \det(\mathbf{1}) = 1 \tag{1.1.43}$$

thus

$$\det\left(\mathbf{A}^{-1}\right) = \det(\mathbf{A})^{-1} \tag{1.1.44}$$

8.

$$\mathbf{A}\mathbf{A}^{\dagger} = \mathbf{1} \Rightarrow \det(\mathbf{A})\det\left(\mathbf{A}^{\dagger}\right) = \det(\mathbf{1}) = 1 \tag{1.1.45}$$

From Ex 1.5.4, we have

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

9. From Ex 1.5.5, we get

$$\det\left(\mathbf{U}^{\dagger}\right)\det(\mathbf{O})\det(\mathbf{U}) = \det(\mathbf{\Omega}) \tag{1.1.47}$$

and

$$\det\left(\mathbf{U}^{\dagger}\right)\det(\mathbf{U}) = \det(\mathbf{1}) = 1 \tag{1.1.48}$$

$\therefore$

$$\det(\mathbf{O}) = \det(\mathbf{\Omega}) \tag{1.1.49}$$

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

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{c} = \mathbf{0} \Rightarrow \mathbf{c} = \mathbf{0} \tag{1.1.50}$$

□

1.1.4 N-D Complex Vector Spaces

1.1.5 Change of Basis

Ex 1.8

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

gives

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

1.1.6 The Eigenvalue Problem

Ex 1.9

$$\mathbf{O}\mathbf{U} = \mathbf{U}\boldsymbol{\omega} \Rightarrow \mathbf{O}\begin{pmatrix}\mathbf{c}^1 & \mathbf{c}^2 & \cdots & \mathbf{c}^N\end{pmatrix} = \begin{pmatrix}\omega_1\mathbf{c}_1 & \omega_2\mathbf{c}_2 & \cdots & \omega_N\mathbf{c}_N\end{pmatrix} \tag{1.1.53}$$

thus

$$\mathbf{O}\mathbf{c}^{\alpha} = \omega_{\alpha}\mathbf{c}^{\alpha} \tag{1.1.54}$$

Ex 1.10

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

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

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

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

Ex 1.11

a)

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

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \tag{1.1.60}$$

Eigenvectors

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

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

Eigenvalues

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

Eigenvectors

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

b)

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

for **A**

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

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \tag{1.1.67}$$

Eigenvectors

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

for **B**

$$\theta_0 = \frac{1}{2}\tan^{-1}\frac{2\times 1}{3-2} = \frac{1}{2}\tan^{-1} 2 \tag{1.1.69}$$

Eigenvalues

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

Eigenvectors

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

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

Details are in `1-1.nb`

1.1.7 Functions of Matrices

Ex 1.12

a.

$$\mathbf{A}^n = \mathbf{U}\mathbf{a}^n\mathbf{U}^\dagger \tag{1.1.73}$$

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

b. From 1.4.a, we have

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

c.

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

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

while

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

thus

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

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

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

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

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

$$\omega_1 = a - b \quad \omega_2 = a + b \tag{1.1.82}$$

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

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

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

1.2 Orthogonal Functions, Eigenfunctions, and Operators

Ex 1.14

$$\int_{-\infty}^{\infty} \mathrm{d}x a(x)\delta(x) = \lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon} \mathrm{d}x a(x)\frac{1}{2\varepsilon} = \lim_{\varepsilon\to 0}\frac{1}{2\varepsilon}\int_{-\varepsilon}^{\varepsilon} \mathrm{d}x a(x) \xlongequal{\text{L'Hôpital}} \lim_{\varepsilon\to 0}\frac{a(\varepsilon)-[-a(-\varepsilon)]}{2} = a(0) \tag{1.2.1}$$

Ex 1.15

$$\begin{aligned}\int \mathrm{d}x\psi_j^*(x)\mathcal{O}\psi_i(x) &= \int \mathrm{d}x\psi_j^*(x)\sum_k \psi_k(x)O_{ki} = \sum_k O_{ki}\int \mathrm{d}x\psi_j^*(x)\psi_k(x) \\ &= \sum_k O_{ki}\delta_{jk} = O_{ji}\end{aligned} \tag{1.2.2}$$

In bra-ket notation, (1) becomes

$$\mathcal{O}\left|i\right\rangle = \sum_j \left|j\right\rangle \left\langle j\,|\,\mathcal{O}\,|\,i\right\rangle \tag{1.2.3}$$

which is identical to Eq.(1.55) in the textbook.

Ex 1.16 With bra-ket notation,

$$\mathcal{O}\sum_{\mathrm{i}=1}^{\infty} c_i\left|i\right\rangle = \omega\sum_{\mathrm{i}=1}^{\infty} c_i\left|i\right\rangle \tag{1.2.4}$$

Multiply by $\langle j|$

$$\sum_{\mathrm{i}=1}^{\infty} c_i\left\langle j\,|\,\mathcal{O}\,|\,i\right\rangle = \omega\sum_{\mathrm{i}=1}^{\infty} c_i\left\langle j\,|\,i\right\rangle = \omega c_j \tag{1.2.5}$$

i.e.

$$\sum_{\mathrm{i}=1}^{\infty} O_{ji}c_i = \omega c_j \tag{1.2.6}$$

$$\mathbf{Oc} = \omega\mathbf{c} \tag{1.2.7}$$

It's similar to prove that without bra-ket notation.

Ex 1.17

a.

$$\int \mathrm{d}x\left\langle i|x\right|\left\langle x\,|\,j\right\rangle = \left\langle i\,|\,j\right\rangle = \delta_{ij} \tag{1.2.8}$$

i.e.

$$\int \mathrm{d}x\psi_i^*(x)\Psi_j(x) = \delta_{ij} \tag{1.2.9}$$

b.

$$\sum_{\mathrm{i}=1}^{\infty}\left\langle x\,|\,i\right\rangle\left\langle i\,|\,x'\right\rangle = \left\langle x\,|\,x'\right\rangle = \delta(x-x') \tag{1.2.10}$$

thus

$$\sum_{\mathrm{i}=1}^{\infty}\psi_i^*(x)\psi_i(x') = \sum_{\mathrm{i}=1}^{\infty}\left\langle x\,|\,i\right\rangle\left\langle i\,|\,x'\right\rangle = \delta(x-x') \tag{1.2.11}$$

c.

$$\int \mathrm{d}x\left\langle x'\,|\,x\right\rangle\left\langle x\,|\,a\right\rangle = \left\langle x'\,|\,a\right\rangle \tag{1.2.12}$$

thus

$$\int \mathrm{d}x\delta(x'-x)a(x) = a(x') \tag{1.2.13}$$

i.e.

$$\int \mathrm{d}x'\delta(x-x')a(x') = a(x) \tag{1.2.14}$$

d.

$$\langle x' \mid \mathcal{O} \mid a \rangle = \int \mathrm{d}x \, \langle x' \mid \mathcal{O} \mid x \rangle \langle x \mid a \rangle = \langle x' \mid b \rangle \tag{1.2.15}$$

$\therefore$

$$\mathcal{O}a(x') = \int \mathrm{d}x O(x', x) a(x) = b(x') \tag{1.2.16}$$

i.e.

$$b(x) = \mathcal{O}a(x) = \int \mathrm{d}x' O(x, x') a(x') \tag{1.2.17}$$

e.

$$\begin{aligned} O(x, x') = \langle x \mid \mathcal{O} \mid x' \rangle &= \langle x | \left(\sum_i |i\rangle \langle i| \right) \mathcal{O} \left(\sum_j |j\rangle \langle j| \right) |x'\rangle \\ &= \sum_{ij} \langle x \mid i \rangle \langle i \mid \mathcal{O} \mid j \rangle \langle j \mid x' \rangle \\ &= \sum_{ij} \psi_i(x) O_{ij} \psi_j^*(x') \end{aligned} \tag{1.2.18}$$

1.3 The Variation Method

1.3.1 The Variation Principle

Ex 1.18

$$\begin{aligned} \mathscr{E} &= \frac{\left\langle \tilde{\Phi} \middle| -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \delta(x) \middle| \tilde{\Phi} \right\rangle}{\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle} = \frac{N^2 \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{-\alpha x^2} \left[-\frac{1}{2}(-2\alpha + 4\alpha^2 x^2) - \delta(x) \right] \mathrm{e}^{-\alpha x^2}}{N^2 \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{-2\alpha x^2}} \\ &= \frac{\alpha \dfrac{\pi^{1/2}}{(2\alpha)^{1/2}} - 2\alpha^2 \dfrac{2\pi^{1/2}}{4(2\alpha)^{3/2}} - 1}{\dfrac{\pi^{1/2}}{(2\alpha)^{1/2}}} \\ &= \frac{\alpha\pi^{1/2} - \alpha^2 \dfrac{\pi^{1/2}}{(2\alpha)} - (2\alpha)^{1/2}}{\pi^{1/2}} \\ &= \alpha - \frac{1}{2}\alpha - \frac{(2\alpha)^{1/2}}{\pi^{1/2}} \\ &= \frac{1}{2}\alpha - \frac{(2\alpha)^{1/2}}{\pi^{1/2}} \end{aligned} \tag{1.3.1}$$

Let $\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\alpha} = 0$, we have

$$\frac{1}{2} - \frac{1}{(2\pi\alpha)^{1/2}} = 0 \Rightarrow \alpha = \frac{2}{\pi} \tag{1.3.2}$$

thus

$$\mathscr{E}_{min} = -\frac{1}{\pi} \tag{1.3.3}$$

Ex 1.19

$$
\begin{aligned}
\mathscr{E} = \frac{\left\langle \tilde{\Phi} \middle| -\frac{1}{2}\nabla^2 - \frac{1}{r} \middle| \tilde{\Phi} \right\rangle}{\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle} &= \frac{N^2 \cdot 4\pi \int_{-\infty}^{\infty} r^2 \mathrm{d}r\, \mathrm{e}^{-\alpha r^2} \left[-\frac{1}{2}(4\alpha^2 r^2 - 6\alpha) - \frac{1}{r} \right] \mathrm{e}^{-\alpha r^2}}{N^2 \cdot 4\pi \int_{-\infty}^{\infty} r^2 \mathrm{d}r\, \mathrm{e}^{-2\alpha r^2}} \\
&= \frac{-2\alpha^2 \frac{24\pi^{1/2}}{64(2\alpha)^{5/2}} + 3\alpha \frac{2\pi^{1/2}}{8(2\alpha)^{3/2}} - \frac{1}{2(2\alpha)}}{\frac{2\pi^{1/2}}{8(2\alpha)^{3/2}}} \\
&= -2\alpha^2 \frac{12}{8(2\alpha)} + 3\alpha - \frac{2(2\alpha)^{1/2}}{\pi^{1/2}} \\
&= \frac{3}{2}\alpha - \frac{2(2\alpha)^{1/2}}{\pi^{1/2}}
\end{aligned} \tag{1.3.4}
$$

Let $\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}r} = 0$,

$$\frac{3}{2} - \frac{2}{\sqrt{2\pi\alpha}} = 0 \Rightarrow \alpha = \frac{8}{9\pi} \tag{1.3.5}$$

$$\mathscr{E}_{min} = \frac{4}{3\pi} - \frac{8}{3\pi} = -\frac{4}{3\pi} \tag{1.3.6}$$

Ex 1.20

$$
\begin{aligned}
\omega(\theta) = \mathbf{c}^\dagger \mathbf{O} \mathbf{c} &= \begin{pmatrix} \cos\theta & \sin\theta \end{pmatrix} \begin{pmatrix} O_{11}\cos\theta + O_{12}\sin\theta \\ O_{12}\cos\theta + O_{22}\sin\theta \end{pmatrix} \\
&= O_{11}\cos^2\theta + 2O_{12}\cos\theta\sin\theta + O_{22}\sin^2\theta
\end{aligned} \tag{1.3.7}
$$

Let $\frac{\mathrm{d}\omega}{\mathrm{d}\theta} = 0$, thus

$$O_{11}(-2\cos\theta\sin\theta) + O_{12} \cdot 2\cos 2\theta + O_{22} \cdot 2\sin\theta\cos\theta = 0 \tag{1.3.8}$$

$$(O_{22} - O_{11})\sin 2\theta + 2O_{12}\cos 2\theta = 0 \tag{1.3.9}$$

$$\theta = \frac{1}{2}\arctan\frac{2O_{12}}{O_{11} - O_{22}} \tag{1.3.10}$$

$$\omega = O_{11}\cos^2\theta + O_{12}\sin 2\theta + O_{22}\sin^2\theta \tag{1.3.11}$$

which are exactly the results in Eq. (1.105) and Eq. (1.106a) in the textbook. We get the result because the trial vector $\mathbf{c}$ is the exact eigenvector of $\mathbf{O}$.

1.3.2 The Linear Variational Problem

Ex 1.21

a.

$$\left\langle \tilde{\Phi}' \middle| \tilde{\Phi}' \right\rangle = 1 = \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \langle \Phi_\alpha \mid \Phi_\beta \rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \tag{1.3.12}$$

Since $\left\langle \tilde{\Phi}' \middle| \Phi_0 \right\rangle = 0$, we have

$$\sum_{\alpha=1}^{\infty}\sum_{\beta=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \langle \Phi_\alpha \mid \Phi_\beta \rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.13}$$

thus

$$\sum_{\alpha=1}^{\infty}\sum_{\beta=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \delta_{\alpha\beta} \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.14}$$

$$\sum_{\alpha=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \left\langle \Phi_\alpha \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.15}$$

$$\sum_{\alpha=1}^{\infty}\left|\left\langle\Phi_\alpha\,\middle|\,\tilde{\Phi}'\right\rangle\right|^2=1 \tag{1.3.16}$$

Similarly,

$$\left\langle\tilde{\Phi}'\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}'\right\rangle=\sum_{\alpha\beta}\left\langle\tilde{\Phi}'\,\middle|\,\Phi_\alpha\right\rangle\langle\Phi_\alpha\,|\,\mathscr{H}\,|\,\Phi_\beta\rangle\left\langle\Phi_\beta\,\middle|\,\tilde{\Phi}'\right\rangle=\sum_{\alpha=1}^{\infty}\sum_{\beta=1}^{\infty}\left\langle\tilde{\Phi}'\,\middle|\,\Phi_\alpha\right\rangle\langle\Phi_\alpha\,|\,\mathscr{H}\,|\,\Phi_\beta\rangle\left\langle\Phi_\beta\,\middle|\,\tilde{\Phi}'\right\rangle \tag{1.3.17}$$

From Eq. (1.170) from the textbook, we get

$$\langle\Phi_\alpha\,|\,\mathscr{H}\,|\,\Phi_\beta\rangle=\mathscr{E}_\alpha\delta_{\alpha\beta} \tag{1.3.18}$$

thus

$$\left\langle\tilde{\Phi}'\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}'\right\rangle=\sum_{\alpha=1}^{\infty}\left|\left\langle\Phi_\alpha\,\middle|\,\tilde{\Phi}'\right\rangle\right|^2\mathscr{E}_\alpha\geq\sum_{\alpha=1}^{\infty}\left|\left\langle\Phi_\alpha\,\middle|\,\tilde{\Phi}'\right\rangle\right|^2\mathscr{E}_1=\mathscr{E}_1 \tag{1.3.19}$$

b.

$$\left\langle\tilde{\Phi}'\,\middle|\,\tilde{\Phi}'\right\rangle=1=\left(x^*\langle\tilde{\Phi}_0|+y^*\langle\tilde{\Phi}_1|\right)\left(x|\tilde{\Phi}_0\rangle+y|\tilde{\Phi}_1\rangle\right)=|x|^2+|y|^2 \tag{1.3.20}$$

c.

$$\begin{aligned}\left\langle\tilde{\Phi}'\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}'\right\rangle&=|x|^2\left\langle\tilde{\Phi}_0\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}_0\right\rangle+|y|^2\left\langle\tilde{\Phi}_1\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}_1\right\rangle+x^*y\left\langle\tilde{\Phi}_0\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}_1\right\rangle+xy^*\left\langle\tilde{\Phi}_1\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}_0\right\rangle\\&=E_1-|x|^2(E_1-E_0)\end{aligned} \tag{1.3.21}$$

thus

$$\mathscr{E}_1\leq\left\langle\tilde{\Phi}'\,\middle|\,\mathscr{H}\,\middle|\,\tilde{\Phi}'\right\rangle\leq E_1-|x|^2(E_1-E_1)=E_1 \tag{1.3.22}$$

Ex 1.22

$$\begin{aligned}H_{11}&=\langle 1s\,|\,\mathscr{H}\,|\,1s\rangle=-\frac{1}{2}+F\langle 1s\,|\,r\cos\theta\,|\,1s\rangle=-\frac{1}{2}\\H_{12}&=H_{21}=\langle 1s\,|\,\mathscr{H}\,|\,2p_z\rangle=0+F\langle 1s\,|\,r\cos\theta\,|\,2p_z\rangle=\frac{128\sqrt{2}\pi}{243}F\\H_{22}&=\langle 2p_z\,|\,\mathscr{H}\,|\,2p_z\rangle=-\frac{1}{8}+F\langle 2p_z\,|\,r\cos\theta\,|\,2p_z\rangle=-\frac{1}{8}\end{aligned} \tag{1.3.23}$$

Suppose $\mathbf{c}=\begin{pmatrix}\cos p\\ \sin p\end{pmatrix}$, with the result of Ex 1.20, we have

$$p=\frac{1}{2}\arctan\frac{2H_{12}}{H_{11}-H_{22}}=-\frac{1}{2}\arctan\left(\frac{2048\sqrt{2}F}{729}\right) \tag{1.3.24}$$

thus

$$\mathscr{E}(F)=H_{11}\cos^2 p+H_{12}\sin 2p+H_{22}\sin^2 p=-\frac{1}{2}-\frac{262144}{177147}F^2+\mathcal{O}(F^3) \tag{1.3.25}$$

$\therefore$

$$\alpha=2\times\frac{262144}{177147}=2.96 \tag{1.3.26}$$