Selected Exercises from ***Modern Quantum Chemistry Introduction to Advanced Electronic Structure Theory*** © 1996 by Attila Szabo and Neil S. Ostlund (Dover Books)

Exercise 1.1 a) For concreteness I use a 3x3 operator (1x3)(3x3)(3x1) = (1x3)(3x1)=(1x1):

$$[e_1 \quad e_2 \quad e_3]\begin{bmatrix} O_{11} & O_{12} & O_{13} \\ O_{21} & O_{22} & O_{23} \\ O_{31} & O_{32} & O_{33} \end{bmatrix}\begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix}$$

$$= [e_1 O_{11} + e_2 O_{21} + e_3 O_{31} \quad e_1 O_{12} + e_2 O_{22} + e_3 O_{32} \quad e_1 O_{13} + e_2 O_{23} + e_3 O_{33}]\begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix}$$

$$= [e_1 O_{11} e_1 + e_2 O_{21} e_1 + e_3 O_{31} e_1 \quad e_1 O_{12} e_2 + e_2 O_{22} e_2 + e_3 O_{32} e_2 \quad e_1 O_{13} e_1 + e_2 O_{23} e_2 + e_3 O_{33} e_3]$$

b) (3x3)(3x1)=(3x1)

$$\begin{bmatrix} O_{11} & O_{12} & O_{13} \\ O_{21} & O_{22} & O_{23} \\ O_{31} & O_{32} & O_{33} \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}$$

$$\begin{bmatrix} O_{11}a_1 + O_{12}a_2 + O_{13}a_3 \\ O_{21}a_1 + O_{22}a_2 + O_{23}a_3 \\ O_{31}a_1 + O_{32}a_2 + O_{33}a_3 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}$$

Exercise 1.2

$$[A, B] = AB - BA$$

$$\{A, B\} = AB + BA$$

I wrote a little computer program to solve some of these exercises (483 lines of C++ source code):

```
Matrix A:
 1.00    1.00    0.00
 1.00    2.00    2.00
 0.00    2.00   -1.00
Matrix B:
 1.00   -1.00    1.00
-1.00    0.00    0.00
 1.00    0.00    1.00
Commutator:
 0.00    0.00   -2.00
 0.00   -2.00    3.00
-2.00    3.00   -2.00
Anti-commutator:
 0.00   -2.00    4.00
 2.00    0.00    3.00
-4.00   -3.00    0.00
```

Exercise 1.3

Matrix A:

```
  +1    +1    +0
  +1    +2    +2
  +0    +2    -1
```

Matrix B:

```
  +1    -1    +1
  -1    +0    +0
  +1    +0    +1
```

Commutator:

```
  +0    +0    -2
  +0    -2    +3
  -2    +3    -2
```

Anti-commutator:

```
  +0    -2    +4
  +2    +0    +3
  -4    -3    +0
```

Matrix A:

```
  +1    +7i   +4    +0i
  +9    +4i   +8    +8i
  +2    +4i   +5    +5i
```

Matrix B:

```
  +1    +7i   +1    +1i   +5    +2i   +7    +6i
  +1    +4i   +2    +3i   +2    +2i   +1    +6i
```

Matrix AB:

```
 -44   +30i   +2   +20i   -1   +45i  -31   +79i
 -43  +107i   -3   +53i  +37   +70i   -1  +138i
 -41   +43i   -7   +31i   +2   +44i  -35   +75i
```

```
Matrix A-Adjoint:

  +1    -7i   +9    -4i   +2    -4i
  +4    -0i   +8    -8i   +5    -5i

Matrix B-Adjoint:

  +1    -7i   +1    -4i
  +1    -1i   +2    -3i
  +5    -2i   +2    -2i
  +7    -6i   +1    -6i

Matrix AB-Adjoint:

 -44   -30i  -43  -107i  -41   -43i
  +2   -20i   -3   -53i   -7   -31i
  -1   -45i  +37   -70i   +2   -44i
 -31   -79i   -1  -138i  -35   -75i

Matrix B-Adjoint A-Adjoint:

 -44   -30i  -43  -107i  -41   -43i
  +2   -20i   -3   -53i   -7   -31i
  -1   -45i  +37   -70i   +2   -44i
 -31   -79i   -1  -138i  -35   -75i

Complex adjoints are equal
```

Exercise 1.4

a.

$$\boldsymbol{tr}(\boldsymbol{AB}) = \sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \boldsymbol{A_{ik}B_{jk}} = \sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \boldsymbol{A_{ii}B_{ii}} = \sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \boldsymbol{B_{ii}A_{ii}} = \boldsymbol{tr}\left(\sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \boldsymbol{B_{ik}A_{kj}}\right) = \boldsymbol{tr}(\boldsymbol{BA})$$

Where we have used the commutative properties of real and complex numbers.

b.

$$AA^{-1} = I$$

$$BAA^{-1}B^{-1} = BIB^{-1} = I$$

$$A^{-1}B^{-1} = (BA)^{-1} = (AB\ )^{-1}$$

$$A = \begin{pmatrix} 1 & 3 \\ 3 & 4 \end{pmatrix}$$

$$A^{-1} = -\frac{1}{5}\begin{pmatrix} 4 & -3 \\ -3 & 1 \end{pmatrix}$$

$$B = \begin{pmatrix} 5 & 6 \\ 6 & 8 \end{pmatrix}$$

$$B^{-1} = \frac{1}{4}\begin{pmatrix} 8 & -6 \\ -6 & 5 \end{pmatrix}$$

$$A^{-1}B^{-1} = -\frac{1}{20}\begin{pmatrix} 4 & -3 \\ -3 & 1 \end{pmatrix}\begin{pmatrix} 8 & -6 \\ -6 & 5 \end{pmatrix} = -\frac{1}{20}\begin{pmatrix} 32+18 & -24-15 \\ -24-6 & 18+5 \end{pmatrix} = -\frac{1}{20}\begin{pmatrix} 50 & 39 \\ -30 & 23 \end{pmatrix}$$

$$AB = \begin{pmatrix} 1 & 3 \\ 3 & 4 \end{pmatrix}\begin{pmatrix} 5 & 6 \\ 6 & 8 \end{pmatrix} = \begin{pmatrix} 5+18 & 6+24 \\ 15+24 & 18+32 \end{pmatrix} = \begin{pmatrix} 23 & 30 \\ 39 & 50 \end{pmatrix}$$

$$(AB\ )^{-1} = \frac{1}{23 \cdot 50 - 30 \cdot 39}\begin{pmatrix} 50 & -30 \\ -39 & 23 \end{pmatrix} = -\frac{1}{20}\begin{pmatrix} 50 & -30 \\ -39 & 23 \end{pmatrix}$$

c.

$$B = U^{\perp}AU$$

$$A = UBU^{\perp}$$

$$UBU^{\perp} = UU^{\perp}AUU^{\perp} = UU^{\perp}A = A$$

f.

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix} = \begin{pmatrix} A_{11}A_{22} - A_{12}A_{21} & A_{21}A_{22} - A_{22}A_{21} \\ -A_{11}A_{12} + A_{12}A_{11} & -A_{21}A_{12} + A_{22}A_{11} \end{pmatrix}$$
$$= \begin{pmatrix} A_{11}A_{22} - A_{12}A_{21} & 0 \\ 0 & A_{11}A_{22} - A_{12}A_{21} \end{pmatrix}$$

$$A^{-1}A = AA^{-1} = \frac{A}{|A|} = \frac{A}{A_{11}A_{22} - A_{12}A_{21}}$$

Exercise 1.5

$$\begin{vmatrix} 0 & 0 \\ 1 & 1 \end{vmatrix} = 0 - 0 = 0, same\ holds\ for\ a\ zero\ column$$

$$\begin{vmatrix} A_{11} & 0 \\ 0 & A_{22} \end{vmatrix} = A_{11}A_{22}$$

$$\begin{vmatrix} A_{21} & A_{22} \\ A_{11} & A_{12} \end{vmatrix} = A_{21}A_{12} - A_{22}A_{11} = -(A_{22}A_{11} - A_{21}A_{12}) = \begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix}$$

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix}\begin{vmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{vmatrix} = (A_{11}A_{22} - A_{12}A_{21})(B_{11}B_{22} - B_{12}B_{21})$$
$$= A_{11}B_{11}A_{22}B_{22} - A_{11}B_{12}A_{22}B_{21} - A_{12}B_{11}A_{21}B_{22} + A_{12}B_{12}A_{21}B_{21}$$

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{pmatrix} A_{11}B_{11} + A_{12}B_{21} & A_{11}B_{12} + A_{12}B_{22} \\ A_{21}B_{11} + A_{22}B_{21} & A_{21}B_{12} + A_{22}B_{22} \end{pmatrix}$$

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

Exercise 1.8

```
Matrix A:

    +7.000000      +4.000000
    +0.000000      +9.000000

    +4.000000      +8.000000
    +8.000000      +2.000000

    +4.000000      +5.000000
    +5.000000      +1.000000


Matrix B:

    +7.000000      +1.000000
    +1.000000      +5.000000
    +2.000000      +7.000000
    +6.000000      +1.000000

    +4.000000      +2.000000
    +3.000000      +2.000000
    +2.000000      +1.000000
    +6.000000      +8.000000


Matrix AB:

   +27.000000     +71.000000
   -31.000000     +66.000000
   -23.000000     +75.000000
   -34.000000     +85.000000

   +48.000000     +84.000000
   -16.000000     +50.000000
   -34.000000     +56.000000
   +48.000000    +128.000000
```

```
   +41.000000     +53.000000
    -8.000000     +38.000000
   -18.000000     +45.000000
   +41.000000     +80.000000


Matrix A-Adjoint:

    +7.000000      -4.000000
    +4.000000      -8.000000
    +4.000000      -5.000000

    +0.000000      -9.000000
    +8.000000      -2.000000
    +5.000000      -1.000000


Matrix B-Adjoint:

    +7.000000      -1.000000
    +4.000000      -2.000000

    +1.000000      -5.000000
    +3.000000      -2.000000

    +2.000000      -7.000000
    +2.000000      -1.000000

    +6.000000      -1.000000
    +6.000000      -8.000000


Matrix AB-Adjoint:

   +27.000000     -71.000000
   +48.000000     -84.000000
   +41.000000     -53.000000

   -31.000000     -66.000000
   -16.000000     -50.000000
    -8.000000     -38.000000

   -23.000000     -75.000000
   -34.000000     -56.000000
   -18.000000     -45.000000

   -34.000000     -85.000000
```

```
   +48.000000    -128.000000
   +41.000000     -80.000000


Matrix B-Adjoint A-Adjoint:

   +27.000000     -71.000000
   +48.000000     -84.000000
   +41.000000     -53.000000

   -31.000000     -66.000000
   -16.000000     -50.000000
    -8.000000     -38.000000

   -23.000000     -75.000000
   -34.000000     -56.000000
   -18.000000     -45.000000

   -34.000000     -85.000000
   +48.000000    -128.000000
   +41.000000     -80.000000


Complex adjoints are equal

Matrix U:

    +0.707107      +0.000000
    +0.000000      -0.707107

    +0.707107      +0.000000
    +0.000000      +0.707107


Matrix U-Adjoint:

    +0.707107      -0.000000
    +0.707107      -0.000000

    +0.000000      +0.707107
    +0.000000      -0.707107


Matrix U U-Adjoint:

    +1.000000      +0.000000
    +0.000000      +0.000000
```

```
    +0.000000      +0.000000
    +1.000000      +0.000000


Matrix Omega:

    +5.000000      +7.000000
    +6.000000      +1.000000

    +2.000000      +7.000000
    +9.000000      +5.000000


Matrix U-Adjoint Omega U:

   +11.000000     +10.000000
    +4.000000      +4.000000

    +2.000000      -0.000000
    +3.000000      +2.000000


Trace Omega Real         = 14
Trace Omega Imag         = 12
Trace U-a Omega U Real   = 14
Trace U-a Omega U Imag   = 12
```

Exercise 1.18

$$-\frac{1}{2}\frac{d^2|\Phi\rangle}{dx^2} - \delta(x)|\Phi\rangle = E|\Phi\rangle$$

$$|\Phi\rangle = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha x^2}$$

$$-\frac{1}{2}\left(\frac{2\alpha}{\pi}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\alpha x^2}\frac{d^2 e^{-\alpha x^2}}{dx^2}dx - 1 = E$$

$$\frac{d^2 e^{-\alpha x^2}}{dx^2} = -2\alpha\left(\frac{d}{dx}xe^{-\alpha x^2}\right) = -2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2} \quad \int_{-\infty}^{\infty} e^{-\alpha x^2}\frac{d^2 e^{-\alpha x^2}}{dx^2}dx$$

$$= -2\alpha\int_{-\infty}^{\infty} e^{-2\alpha x^2}dx + 4\alpha^2\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2}dx = -2\alpha\frac{\sqrt{\pi}}{\sqrt{2\alpha}} + 4\alpha^2\frac{2\sqrt{\pi}}{4(2\alpha)^{3/2}}$$

$$N = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

$$E = -\frac{1}{2}N^2\left[-2\alpha\sqrt{\frac{\pi}{2\alpha}} + 4\alpha^2\frac{2\sqrt{\pi}}{4(2\alpha)^{3/2}}\right] = N^2\left[\alpha\sqrt{\frac{\pi}{2\alpha}} - \frac{\alpha^2\sqrt{\pi}}{(2\alpha)^{3/2}}\right] - 1$$

I wrote a little program to minimize the total energy, E. I used the function MININ which does not require a derivative and computes the minimum of a function of a single variable. MININ is from Chapter 5 ***A Numerical Library in C for Scientists and Engineers*** © 1995 by H. T. Lau, PhD. The results are shown after **Exercise 1.19**. QC stands for the quantum chemistry textbook of this document.

Exercise 1.19

$$\frac{d}{dr}e^{-\alpha r^2} = -2\alpha r e^{-\alpha r^2}$$

$$\frac{d}{dr}\left(-2\alpha r^3 e^{-\alpha r^2}\right) = -6\alpha r^2 e^{-\alpha r^2} + 4\alpha^2 r^4 e^{-\alpha r^2}$$

$$E = 3\alpha N^2(4\pi)\int_0^\infty r^2 e^{-2\alpha r^2}dr - \frac{4}{2}\alpha^2 N^2(4\pi)\int_0^\infty r^4 e^{-2\alpha r^2}dr - 4\pi N^2\int_0^\infty r e^{-2\alpha r^2}dr$$

$$E = 3\alpha N^2(4\pi)\frac{2\sqrt{\pi}}{8(2\alpha)^{3/2}} - \frac{4}{2}\alpha^2 N^2(4\pi)\frac{4!\,\sqrt{\pi}}{2^5 2!\,(2\alpha)^{5/2}} - 4\pi N^2\frac{1}{4\alpha}$$

```
Exercise 1.18 Results
My Best Energy      = -0.3307534643
My Best Alpha       = +1.4500000000
My Percent Error    = +33.8493071403
QC Best Energy      = -0.3183098862
Experimental Energy = -0.5000000000
QC Percent Error    = +36.3380227632
Exercise 1.19 Results
My Best Energy      = -0.4244131816
My Best Alpha       = +0.2829421511
My Percent Error    = +15.1173636843
QC Best Energy      = -0.4244131816
Experimental Energy = -0.5000000000
QC Percent Error    = +15.1173636843
```