Homework exercises for the Numerical Linear Algebra part

Please, once you have finished your homework assignment upload your programs (.f90 files), data files (if required) and other required documents (.pdf format) to the Moodle platform before March 10th 2023.

Exercise 1. Linear systems

In this assignment you should write to perform a least square regression analysis to fit a set of points to a polynomial of degree *m*. Your program will need a subroutine, written by yourself, to solve a linear system by the Gauss-Jordan method. Besides your source files (.f90 files) you should also deliver the necessary data files and a .pdf document containing a report including the theoretical background, the description of your program (including pseudocode to discuss the principal algorithms), and a section showing and discussing the results obtained with your program for the examples suggested below. For the discussion you may use other programs/tools to do the fitting and check that your program is working properly. Include also a graphical representation of your data points with the corresponding fitting curves in each case and a list of references. Remember also to include figure captions for all your figures.

Polynomial regression analysis

The least squares regression polynomial of degree m for the points $\{(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)\}$ is given by

$$y = a_m x^m + a_{m-1} x^{m-1} + \cdots + a_2 x^2 + a_1 x + a_0,$$

where the coefficients are determined by the following system of $m + 1$ linear equations.

$$\begin{aligned}
n a_0 + (\Sigma x_i) a_1 + (\Sigma x_i^2) a_2 + \cdots + (\Sigma x_i^m) a_m &= \Sigma y_i \\
(\Sigma x_i) a_0 + (\Sigma x_i^2) a_1 + (\Sigma x_i^3) a_2 + \cdots + (\Sigma x_i^{m+1}) a_m &= \Sigma x_i y_i \\
(\Sigma x_i^2) a_0 + (\Sigma x_i^3) a_1 + (\Sigma x_i^4) a_2 + \cdots + (\Sigma x_i^{m+2}) a_m &= \Sigma x_i^2 y_i \\
&\vdots \\
(\Sigma x_i^m) a_0 + (\Sigma x_i^{m+1}) a_1 + (\Sigma x_i^{m+2}) a_2 + \cdots + (\Sigma x_i^{2m}) a_m &= \Sigma x_i^m y_i
\end{aligned}$$

Write a program that contains a subroutine to read the data for the *n* points to be fitted, another subroutine to set up the augmented matrix by calculating all necessary sums for a polynomial of arbitrary degree *m* (you can limit the value to m ≤ 5), and a subroutine to solve the linear system by using gaussian elimination with pivoting and back-substitution and a subroutine to write the results in a nice format. Look for the expression of the R^2

coefficient to gauge the goodness of your fit and write also a subroutine to calculate this statistical indicator. Write also subroutine to write a file containing the (x,y) values necessary to plot the fitting function (continuous line) and the original data points (markers) using a graphical utility such as GNUplot.

Use your program to solve the following problems:

In Exercises 5–8, find the third-degree least squares regression polynomial for the given data. Then graphically compare the model to the given points.

5. $(0, 0), (1, 2), (2, 4), (3, 1), (4, 0), (5, 1)$

6. $(1, 1), (2, 4), (3, 4), (5, 1), (6, 2)$

7. $(-3, 4), (-1, 1), (0, 0), (1, 2), (2, 5)$

8. $(-7, 2), (-3, 0), (1, -1), (2, 3), (4, 6)$

9. Find the second-degree least squares regression polynomial for the points

$$\left(-\frac{\pi}{2}, 0\right), \left(-\frac{\pi}{3}, \frac{1}{2}\right), (0, 1), \left(\frac{\pi}{3}, \frac{1}{2}\right), \left(\frac{\pi}{2}, 0\right).$$

Then use the results to approximate $\cos(\pi/4)$. Compare the approximation with the exact value.

Exercise 2. Matrix Diagonalization

In this assignment you should write a program to perform Hückel MO calculations for conjugated hydrocarbons with an arbitrary number of carbon atoms. Your program should contain a subroutine written by you to diagonalize real symmetric matrices using the Jacobi method and call it to diagonalize the Hamiltonian matrix to obtain molecular orbital energies (eigenvalues) and coefficients (eigenvectors), the total energy for the π-system (considering the lowest energy configuration where you fill all lower energy MOs with electron pairs plus a single occupied MO for systems with an odd number of electrons) ,and π-electron occupations and bond orders from a Mulliken analysis.

Once finished, use your program to calculate the energies and coefficients of the π-type MOs of the following molecules: 1,3-butadiene, cyclopentadiene anion, benzene, naphthalene, and pyrene. Besides of the program you should also deliver a .pdf file containing a report containing the theoretical background, an explanation of the structure of your program (use pseudocode for the principal algorithms) and a discussion of the results obtained with your program for the molecules above (check that your computed charges agree with the symmetry of your molecule).

The Hückel method

The Hückel method is a very simple linear combination of atomic orbitals (LCAO) molecular orbitals method for the determination of energies of molecular orbitals of π-electrons in π-delocalized molecules, such as ethylene, benzene or butadiene. In the Hückel method we consider a basis of atomic orbitals (AOs) containing just the $2p_z$ orbitals on C atoms and our task is to solve the following set of *n* simultaneous equations:

$$\sum_{j=1}^{n} c_j(H_{ij} - ES_{ij}) = 0 \quad (i = 1, \cdots, n)$$

where *n* is the number of AOs in the basis (= number of C atoms), H_{ij} the elements of the Hamiltonian matrix, S_{ij} those of the overlap matrix, E the eigenvalues and c_j the components of the eigenvectors. Finding nontrivial solutions to the simultaneous equations can be achieved by finding values of E such that:

$$\det([H_{ij} - ES_{ij}]) = 0$$

A problem that is equivalent to diagonalization of matrix **H** if **S** is the identity matrix.

To construct **H** and **S**, in the Hückel method, we assume that the AOs form an orthonormal set, that is **S** is equal to the identity matrix and that **H** is parametrized as

$$H_{ij} = \begin{cases} \alpha, & i = j; \\ \beta, & i, j \text{ adjacent}; \\ 0, & \text{otherwise.} \end{cases}$$

where α and β are two parameters, for which you may use α= -11.4 eV and β = -0.8 eV, respectively.

In order to specify a given molecule you may use an xyz file (look at openbabel.org what the xyz format is if you are not familiar with it) with the cartesian coordinates of your molecule:

```
12
benzene example
  C        0.00000        1.40272        0.00000
  H        0.00000        2.49029        0.00000
  C       -1.21479        0.70136        0.00000
  H       -2.15666        1.24515        0.00000
  C       -1.21479       -0.70136        0.00000
  H       -2.15666       -1.24515        0.00000
  C        0.00000       -1.40272        0.00000
  H        0.00000       -2.49029        0.00000
  C        1.21479       -0.70136        0.00000
  H        2.15666       -1.24515        0.00000
  C        1.21479        0.70136        0.00000
  H        2.15666        1.24515        0.00000
```

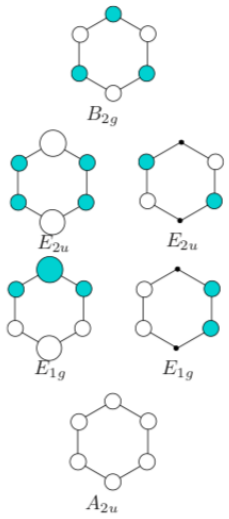
In a first step you must build the distance matrix for the molecule containing the distances for each pair of atoms, and from these, extract a topological or adjacency matrix for the C skeleton with 1 or 0 values if two C atoms are connected or not (use standard distances for C-C bonds to decide if they are connected or not). Note that the topological matrix for benzene will be of dimensions 6x6 while the distance matrix is 12x12, don't get confused, H atoms are not considered in the Hückel method.

Besides of the geometry, you should give also the Hückel parameters, and the charge of the molecule from where you get the number of $\boldsymbol{\pi}$-electrons. Once this is done, use the topological matrix and the Hückel parameters to build the Hamiltonian matrix and diagonalize it to obtain eigenvectors ($\boldsymbol{\pi}$-type MOs) and their corresponding eigenvalues (MO energies).

Check if your eigenvectors are normalized and if this is not the case, normalize them. Be careful with the order in which you get the eigenvectors/values since you will need to fill the MOs, from lower to higher energies, to get the proper occupation numbers to compute the total energy.

Write also the necessary code to perform a Mulliken analysis to obtain $\boldsymbol{\pi}$-electron populations and bond orders (see for instance the Hückel method article in the Wikipedia for the equations).

In your discussion of results please do not include just screenshots with interminable lists of coefficients! You may give the coefficients for small molecules, to check if everything is ok, but it would be nice if you can represent the orbitals graphically, for instance by plotting circles in two colors (for positive/negative) coefficients and the radii of the circles being proportional to the magnitude of the coefficients as in the following picture.



Check also that your results make sense from a chemical point of view, do not simply print lists of numbers coming out from your program!