

Fairly elegant numerical method on computing the molecular orbital ψ and its energy E

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Prolouge: This endeavor emerged from the realms of **Computational Chemistry** and **Modern Organic Chemistry**. Though acquainted with rudiments through Chemistry Olympics, introductory texts merely offered heuristic suppositions, lacking quantitative discourse on their physical essence and heuristic approximations, owing to the absence of exposure to linear algebra in secondary education. Further constrained by collegiate specialization, the author could only probe into it within the confines of Numerical Computational Methodologies. While their contribution may lack the resplendence of grandiose endeavors, it does, however, address persistent inquiries. Should it appear overly simplistic for a significant undertaking, your indulgence is sincerely sought. —Dr.Red 2024

1 Fundamentals on Molecular Orbital

In chemistry, a **molecular orbital** is a mathematical function describing the location and wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The terms atomic orbital and molecular orbital were introduced by *Robert S. Mulliken* in 1932 to mean one-electron orbital wave functions. At an elementary level, they are used to describe the region of space in which a function has a significant amplitude.

For an imprecise, but qualitatively useful, discussion of the molecular structure, the molecular orbitals can be obtained from the "Linear combination of atomic orbitals molecular orbital method" ansatz. Here, the molecular orbitals are expressed as linear combinations of atomic orbitals.

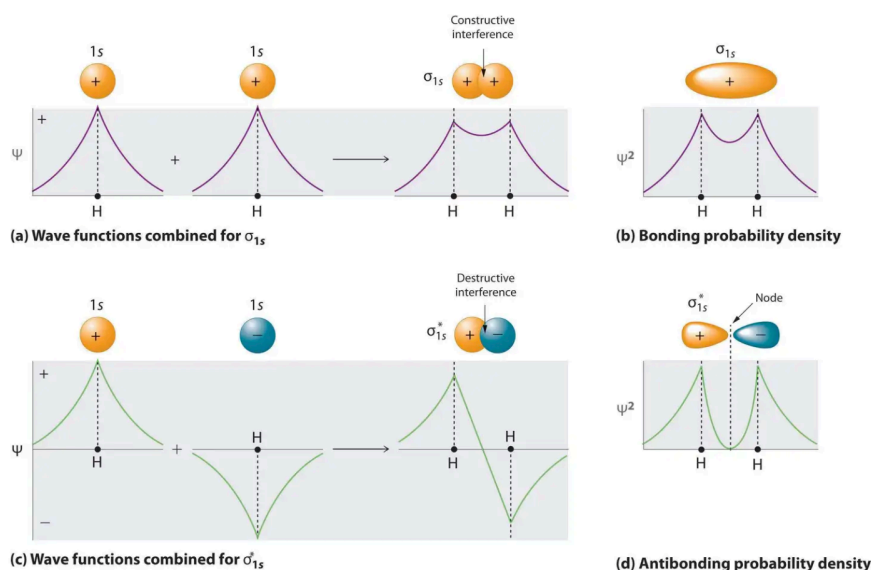


Fig.1 Linear combination of atomic orbitals explanation

More specifically, Linear combinations of atomic orbitals (LCAO) can be used to estimate the molecular orbitals that are formed upon bonding between the molecule's constituent atoms. Similar to an atomic orbital, a Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (1)$$

which describes the behavior of an electron, can be constructed for a molecular orbital as well. Linear combinations of atomic orbitals, or the sums and differences of the atomic wavefunctions, provide approximate solutions to the Hartree–Fock equations

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) + \sum_{j \neq i} \int \frac{e^2 \rho(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j \right) \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i) \quad (2)$$

which correspond to the independent-particle approximation of the molecular Schrödinger equation. For simple diatomic molecules A-B, the wavefunctions obtained are represented mathematically by the equations

$$\begin{cases} \psi = c_1 \phi_A + c_2 \phi_B \\ \psi^* = c_1 \phi_A - c_2 \phi_B \end{cases} \quad (3)$$

Where ψ and ψ^* are described as "bonding" and "anti-bonding" wave functions. ϕ_a and ϕ_b are the orbital wave functions of the constituent atoms, and c_1, c_2 are the coefficients of the linear combination.

2 Secular equation

c_1 and c_2 respectively represent the proportions occupied by the initial orbitals MO in the combined molecular orbital MO. ϕ 's are the results that can be borrowed from atomic orbitals in quantum mechanics (such as obtaining solutions from the hydrogen atom's solutions or wave functions). The value of c 's is unknown. We can use the HF-SCF method to construct the lowest energy wave function to determine the value of c .

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (4)$$

Before applying Eq.3 into the Schrödinger equation, we need to define some of the integrals for the sake of simplicity. First are core integrals defined as

$$\begin{cases} H_{AA} = \langle \phi_A | H | \phi_A \rangle \\ H_{BB} = \langle \phi_B | H | \phi_B \rangle \end{cases} \quad (5)$$

resonance integrals as

$$\begin{cases} H_{AB} = \langle \phi_A | H | \phi_B \rangle \\ H_{BA} = \langle \phi_B | H | \phi_A \rangle \\ H_{AB} = H_{BA} \end{cases} \quad (6)$$

and overlap integrals describing the overlap between the two atomic orbitals

$$\begin{cases} S_{AB} = \langle \phi_A | \phi_B \rangle \\ S_{BA} = \langle \phi_B | \phi_A \rangle \\ S_{AB} = S_{BA} = S \end{cases} \quad (7)$$

It is worth noting that although S_{AA} and S_{BB} are not explicitly defined, they are equal to 1, as the atomic orbitals are normalized. It was beneficial to consider S_{ij} as a element of the S matrix in the following section, which is a symmetric matrix, likewise H_{ij} .

Therefore the energy of the molecular orbital can be expressed as

$$E = \frac{c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}}{c_1^2 + c_2^2 + 2c_1 c_2 S} \quad (8)$$

For any particular molecular geometry (i.e. nuclear configuration: the Born-Oppenheimer approximation) the energy of the ground electronic state is the minimum energy possible for that particular nuclear arrangement and the collection of electrons that goes with it. Hence the following condition,

$$\frac{\partial E}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial E}{\partial c_2} = 0 \quad (9)$$

Which generates such result with elegance,

$$\begin{cases} (H_{AA} - E)c_1 + (H_{AB} - ES_{AB})c_2 = 0 \\ (H_{AB} - ES_{AB})c_1 + (H_{BB} - E)c_2 = 0 \end{cases} \quad (10)$$

To put it more precisely, the above equations can be rewritten as linear matrix equation form as,

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (11)$$

Non-trivial solution for the above equation can be obtained by setting the determinant of the matrix to zero, which is called the Secular equation.

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0 \quad (12)$$

Solve the determinant equation should one obtain,

$$\begin{cases} E_1 = \frac{H_{AA} + H_{AB}}{1 + S} \\ E_2 = \frac{H_{AA} - H_{AB}}{1 - S} \end{cases} \quad (13)$$

Plotting back to the energy equation, one can obtain the coefficients c_1 and c_2 ,

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} k, k \in \mathbb{R} \quad (14)$$

normalize the coefficients by $\langle \psi | \psi \rangle = 1$, one can obtain the final result,

$$\begin{cases} \psi = \frac{1}{\sqrt{2(1+S)}}(\phi_A + \phi_B) \\ \psi^* = \frac{1}{\sqrt{2(1-S)}}(\phi_A - \phi_B) \end{cases} \quad (15)$$

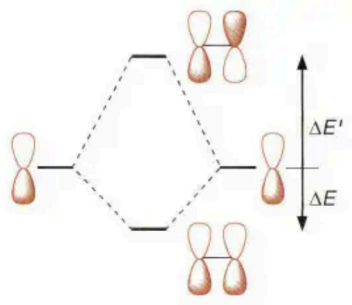


Figure 14.9
A typical MO diagram for mixing two degenerate orbitals, in this case p orbitals.

Fig.2 Textbook level MO representation

likewise, the Secular equation can be extended to the case of polyatomic molecules, where the matrix is of higher dimension.

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - E & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - E \end{vmatrix} = 0$$

3 Hückel method

Observations indicate that the aforementioned expression can be delineated into the following concise and comprehensible matrix format.

$$(H - ES)C = 0 \quad (16)$$

Where

$$H = \begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} & \cdots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} \end{pmatrix} \quad (17)$$

$$S = \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1n} \\ S_{21} & S_{22} & \cdots & S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{n1} & S_{n2} & \cdots & S_{nn} \end{pmatrix} \quad (18)$$

$$C = \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{n1} & c_{n2} & \cdots & c_{nn} \end{pmatrix} \quad (19)$$

Moreover, E could be modified as a diagonal matrix as.

$$E = \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_n \end{pmatrix} \quad (20)$$

Which drastically simplifies the Secular equation to

$$HC = SCE \quad (21)$$

There are many cases where one would solely be interested in the π -orbital energy order. For instance, in aromatic compounds like benzene or pyrrole, the stability and reactivity are primarily governed by the arrangement of π -electrons in aromatic π -orbitals. Analyzing the π -orbital energy order provides insights into the aromatic stabilization energy and the aromatic character of molecules.

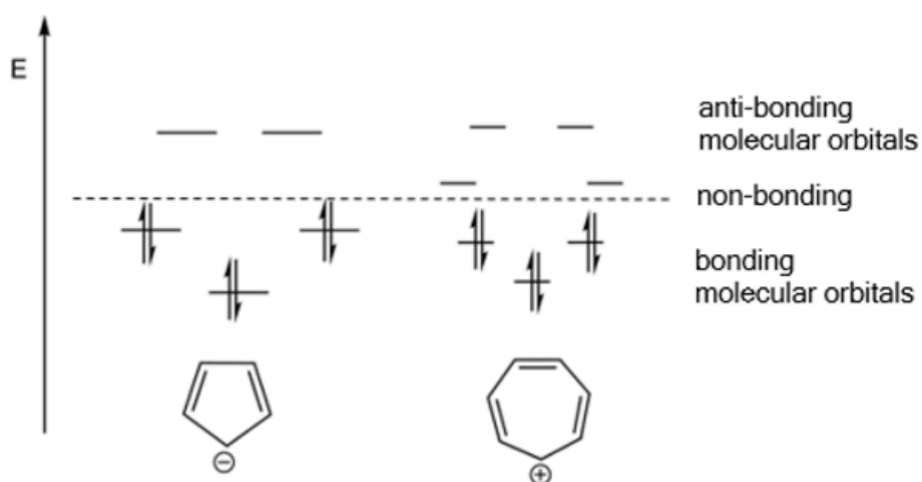


Fig.3 Aromatic compound MO which solely considers π -electrons

For such cases, to further simplify the equation (As the S matrix seems very naucious), one could apply the Hückel theory. The Hückel molecular orbital theory exclusively addresses covalent π -electrons, solely accounting for interactions between nearest neighboring electrons, stipulating orbital overlap S as equal to zero, and disregarding repulsive interactions between electrons. Hence the S matrix is simplified to an identity matrix which further simplified the equation as

$$E = C^T H C \quad (22)$$

Which implied that the energy of the molecular orbital can be obtained by diagonalizing the Hamiltonian matrix H , i.e. finding the **eigenvalues** of the matrix. The corresponding eigenvectors are the coefficients of the linear combination of atomic orbitals that form the molecular orbitals.

4 Implementation

By juxtaposing specific examples through dual methodologies, we can enhance our comprehension of the superior efficacy of linear algebraic approaches in addressing this issue, as well as the inherent efficacy of the Hückel method itself in simplifying such problems.

- **Question** Simple Hückel method usually ignores the Coulomb integral $H_{ii} = \alpha$, which is the energy of the π -orbital itself. It also assumes the resonance integral $H_{ij} = \beta$ is the same 1 for all bonds. With this understanding in place, let us employ the Simple Hückel method to compute the orbital energies and linear combinations of orbital wave functions for the following fulvene.

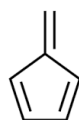


Fig.4 Fulvene molecule

4.1 Theoretical viewpoint

Question

Two methodologies could be applied on this matter. The first is the conventional method, which involves solving the Secular equation. The second is the linear algebraic method, which involves solving the eigenvalues of the matrix. Following the aforementioned premise, we can first derive the Hamiltonian matrix for this molecule

$$H = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

Traditional approaches would involve solving the Secular equation as follows

$$\begin{vmatrix} -E & 1 & 0 & 0 & 1 & 0 \\ 1 & -E & 1 & 0 & 0 & 0 \\ 0 & 1 & -E & 1 & 0 & 0 \\ 0 & 0 & 1 & -E & 1 & 0 \\ 1 & 0 & 0 & 1 & -E & 1 \\ 0 & 0 & 0 & 0 & 1 & -E \end{vmatrix} = 0$$

Question

hence the equation

$$E^6 - 6E^4 + 8E^2 - 2E - 1 = 0$$

Which could be solved by various root-finding algorithm. In this case, **secant method**.

Algorithm 1: Secant Method

Input : Function f , Initial guesses x_0 and x_1 , Tolerance tol

Output: Approximation to the root

```

i ← 2;
y0 ←  $f(x_0)$ ;
y1 ←  $f(x_1)$ ;
while  $|x_i - x_{i-1}| > tol$  do
     $x_i \leftarrow x_{i-1} - y_{i-1} \times \frac{x_{i-1} - x_{i-2}}{y_{i-1} - y_{i-2}};$ 
     $y_i \leftarrow f(x_i);$ 
     $i \leftarrow i + 1;$ 
end
```

For linear algebraic methods, there's little to elaborate on; it suffices to employ a singular approach to compute its eigenvalues and eigenvectors. This can be accomplished through the Lanczos method for real symmetric matrices. The pseudo code for this process is as follows:

Algorithm 2: Lanczos Algorithm for Eigenvalue Computation

Input : Symmetric matrix A , Integer k

Output: Eigenvalues, Eigenvectors

```

n ← dimensions of  $A$ ;
Initialize matrix  $Q$  of size  $n \times k$ ;
Initialize vectors  $\alpha$  and  $\beta$  of size  $k$ ;
Initialize vector  $r_0$  as a random vector of size  $n$ ;
 $r_0 \leftarrow r_0 / \|r_0\|;$ 
 $Q(:, 1) \leftarrow r_0;$ 
for  $j \leftarrow 1$  to  $k$  do
    if  $j == 1$  then
         $v \leftarrow A \times Q(:, j);$ 
    end
    else
         $v \leftarrow A \times Q(:, j) - \beta(j-1) \times Q(:, j-1);$ 
    end
     $\alpha(j) \leftarrow Q(:, j)^T \times v;$ 
     $v \leftarrow v - \alpha(j) \times Q(:, j);$ 
    if  $j < k$  then
         $\beta(j) \leftarrow \|v\|;$ 
         $Q(:, j+1) \leftarrow v / \beta(j);$ 
    end
end
Solve the tridiagonal eigenvalue problem;
 $[T, D] \leftarrow \text{eig}(\text{diag}(\alpha) + \text{diag}(\beta, 1) + \text{diag}(\beta, -1));$ 
Eigenvalues ←  $\text{diag}(D)$ ;
Eigenvectors ←  $Q \times T$ ;
```

4.2 Traditional method: Root-finding

plot the equation $E^6 - 6E^4 + 8E^2 - 2E - 1 = 0$ would one obtain

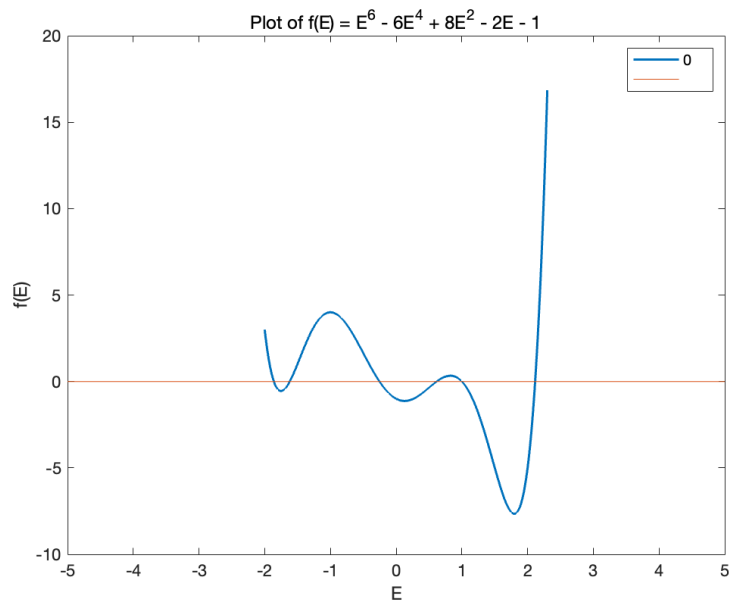


Fig 5. Graph of the equation

The graph implies the section point sets as $x_{sec} = [-2.5, -1.8, -1, 0, 0.8, 1.8, 2.2]$. Applying the multi-section secant method as follows

//Rootfinding_2.m

```

1 clear;
2 clc;
3
4 % Define the function
5 fun = @(E) E.^6 - 6*E.^4 + 8*E.^2 - 2*E - 1;
6
7 f = 0;
8
9 % Generate a range of values for E
10 E = linspace(-2, 2.3, 1000);
11
12 % Evaluate the function
13 y = fun(E);
14
15 % Plot the function
16 figure;
17 plot(E, y, 'LineWidth', 1.5);
18 legend('function')
19 legend('0')
20
21 hold on
22 fplot(f)
23 xlabel('E');
24 ylabel('f(E)');
25 title('Plot of f(E) = E^6 - 6E^4 + 8E^2 - 2E - 1');
26
27 % Find roots numerically using fzero
28 roots = zeros(1,6);
29
30 section = [-2.5, -1.8, -1, 0, 0.8, 1.8, 2.2];
31
32 for i = 1:1:6

```

```

33     [roots(i),Iter,ea] = SecantMethod(section(i),section(i+1),0.5e-5,1000,
        fun);
34 end
35
36 % Display the roots
37 disp('Roots:');
38 disp(roots);
    //SecantMethod.m
1  function [root, iterations, ea] = SecantMethod(x0, x1, tolerance,
    max_iterations, func)
2      syms x; % Declare symbolic variable for the function
3
4      % Convert the input function string to a MATLAB function handle
5      f = matlabFunction(sym(func));
6
7      % Initial values
8      x_prev = x0;
9      x_curr = x1;
10     iterations = 0;
11     ea = 100;
12
13     while true
14         iterations = iterations + 1;
15
16         % Secant method formula
17         x_next = x_curr - f(x_curr) * (x_curr - x_prev) / (f(x_curr) - f(
            x_prev));
18
19         if ea ~= 0
20             ea = abs((x_next - x_curr)/x_next)*100;
21         end
22
23         % Check for convergence
24         if ea < tolerance || iterations >= max_iterations
25             root = x_next;
26             break;
27         end
28
29         plot([x_prev,x_curr],[f(x_prev),f(x_curr)],"--o");
30         hold on
31         plot(x_next,0,"-o");
32         if iterations <= 6
33             text(x_next+0.001,0.001,num2str(iterations));
34         end
35
36         x_prev = x_curr;
37         x_curr = x_next;
38     end
39
40     fplot(f,[0.6,0.8]);
41     ylim([-10,4]);
42
43     legend off
44 end

```

Would one obtain a surprisingly satisfying result

$$E = [-1.8608, -1.618, -0.2541, 0.61803, 1, 2.1149]$$

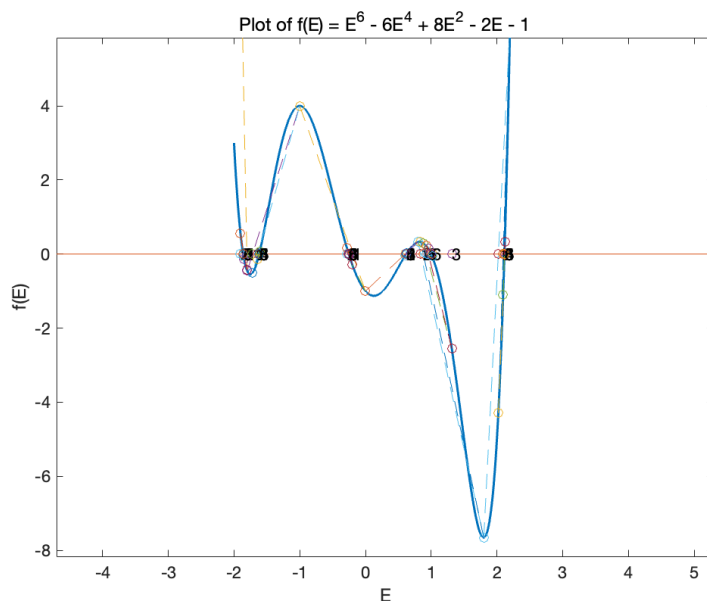


Fig 6. Root-finding result

Substitute back to the Secular equation, one can obtain the coefficients of the linear combination of atomic orbitals that form the molecular orbitals.

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \\ \psi_5 \\ \psi_6 \end{bmatrix} = \begin{bmatrix} -0.44 & 0.15 & 0.15 & -0.44 & 0.66 & -0.36 \\ -0.37 & 0.60 & -0.60 & 0.37 & 0.00 & 0.00 \\ -0.35 & 0.28 & 0.28 & -0.35 & -0.19 & 0.75 \\ -0.60 & 0.37 & -0.37 & -0.60 & -0.00 & 0.00 \\ 0.00 & 0.50 & 0.50 & 0.00 & -0.50 & -0.50 \\ 0.43 & 0.39 & 0.39 & 0.43 & 0.52 & 0.25 \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} \quad (23)$$

Which matches the actual lab results.

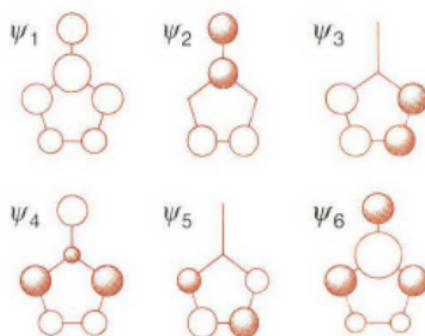


Fig 7. The kind of MO graph that usually appears on the organic chemistry textbook. The 1-6 in the graph corresponds to the 6-1 in the matrix.

4.3 Lanczos Algorithm

The solution of the eigenvalues of the Hamiltonian matrix H is usually not a problem. Apart from the method mention above, one could also use the widely praised QR method to solve the eigenvalues of the matrix. The pseudo code for this process is as follows:

Algorithm 3: QR Algorithm for Eigenvalue Computation

Input : Matrix A , Maximum iterations $max_iterations$, Tolerance tol

Output: Eigenvalues, Eigenvectors

```
 $n \leftarrow$  dimensions of  $A$ ;  
Initialize matrix  $Q$  and matrix  $R$ ;  
Initialize eigenvectors matrix  $V$  as identity matrix of size  $n$ ;  
for  $iter \leftarrow 1$  to  $max\_iterations$  do  
    Compute QR decomposition:  $A = QR$ ;  
     $A \leftarrow R \times Q$ ;  
    Update eigenvectors:  $V \leftarrow V \times Q$ ;  
    Compute off-diagonal elements  $sum\ off\_diag \leftarrow \sum_{i=1}^{n-1} |A(i+1:i, i)|$ ;  
    if  $\max(off\_diag) < tol$  then  
        break;  
    end  
end  
Extract eigenvalues from the diagonal of  $A$ ;  
Eigenvalues  $\leftarrow$  diagonal elements of  $A$ ;
```

In this case, we would use the MATLAB *eig* function instead. It works exactly the same.

The crux of the matter lies in identifying eigenvectors that satisfy the normalization condition for the Hamiltonian matrix, wherein the sum of squares of the norms of all eigenvectors equals 1 (Traditional method sneakily avoided this problem by solving the vector by hand). Typically, eigenvectors yielded by various algorithms for Hamiltonian matrices exhibit fluctuation and instability, potentially failing to meet the requirements of the Hamiltonian matrix.

In this case, the eigenvectors obtained from the Lanczos algorithm are normalized to ensure that the sum of the squares of the norms of all eigenvectors equals 1.

```
1 clear;  
2 clc;  
3  
4 % Define matrix  
5 H =  
    [0,1,0,0,1,0;1,0,1,0,0,0;0,1,0,1,0,0;0,0,1,0,1,0;1,0,0,1,0,1;0,0,0,0,1,0];  
  
6  
7 % Call the lanczos method function  
8 [e1,v1] = lanczos(H, 6);  
9  
10 disp(e1)  
11 disp(v1)  
12  
13 function [eigenvalues, eigenvectors] = lanczos(A, k)  
14     n = size(A, 1);  
15     Q = zeros(n, k);  
16     alpha = zeros(k, 1);  
17     beta = zeros(k - 1, 1);  
18     r0 = rand(n, 1); % Initial random vector  
19     r0 = r0 / norm(r0); % Normalize the initial vector  
20  
21     Q(:, 1) = r0;  
22  
23     for j = 1:k  
24         if j == 1  
25             v = A * Q(:, j);  
26         else  
27             v = A * Q(:, j) - beta(j - 1) * Q(:, j - 1);  
28         end
```

```

29
30     alpha(j) = Q(:, j)' * v;
31     v = v - alpha(j) * Q(:, j);
32
33     if j < k
34         beta(j) = norm(v);
35         Q(:, j + 1) = v / beta(j);
36     end
37 end
38
39 % Solve the tridiagonal eigenvalue problem
40 [T, D] = eig(diag(alpha) + diag(beta, 1) + diag(beta, -1));
41
42 % Eigenvalues
43 eigenvalues = diag(D);
44
45 % Eigenvectors
46 eigenvectors = Q * T;
47 end

```

resulted in the same result as the root-finding method,

$$E = [-1.8608, -1.618, -0.2541, 0.61803, 1, 2.1149]$$

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \\ \psi_5 \\ \psi_6 \end{bmatrix} = \begin{bmatrix} -0.44 & 0.15 & 0.15 & -0.44 & 0.66 & -0.36 \\ -0.37 & 0.60 & -0.60 & 0.37 & 0.00 & 0.00 \\ -0.35 & 0.28 & 0.28 & -0.35 & -0.19 & 0.75 \\ -0.60 & 0.37 & -0.37 & -0.60 & -0.00 & 0.00 \\ 0.00 & 0.50 & 0.50 & 0.00 & -0.50 & -0.50 \\ 0.43 & 0.39 & 0.39 & 0.43 & 0.52 & 0.25 \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} \quad (24)$$

0.43904	-0.37175	0.35054	-0.6015	9.7448e-15	-0.42937
-0.15347	0.6015	-0.27952	-0.37175	0.5	-0.38512
-0.15347	-0.6015	-0.27952	0.37175	0.5	-0.38512
0.43904	0.37175	0.35054	0.6015	9.4406e-15	-0.42937
-0.6635	9.255e-15	0.19044	2.9025e-14	-0.5	-0.52297
0.35657	-5.2302e-16	-0.74948	1.185e-14	-0.5	-0.24728

Fig 7. The more exact result. The minus-positive sign could be flipped over.

This method exhibits a more succinct aspect in addressing highly conjugated molecular systems of substantial π -orbitals compared to conventional polynomial solving approaches, as the following molecule could testify.

5 More complex example

- **Question** Let us consider the following molecule, which is a more complex example of a conjugated system.

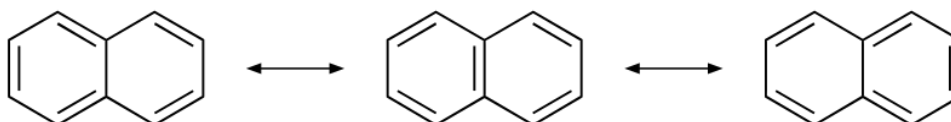


Fig.8 Naphthalene

Compute the orbital energies and linear combinations of orbital wave functions for Naphthalene using the simple Hückel method.

5.1 Analysis

Question

Number the atoms in the molecule from 1 to 10.

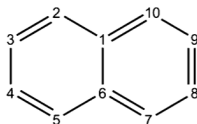


Fig.9 Number the Naphthalene

The Hamiltonian matrix for this molecule is as follows:

$$H = \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ \beta & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha \end{bmatrix}$$

wherein $\alpha = 0$ and $\beta = 1$ for simple Hückel method.

Any attempt to employ conventional methods reliant on determinants of long duration in solving the aforementioned will invariably yield exceedingly intricate determinants and numerical solutions of polynomial equations, or necessitate the application of advanced group-theoretic knowledge for the simplification of the solution process. Such endeavor is notably tedious and of limited generality.

Yet with the linear algebraic approach, the solution is remarkably straightforward. Applying the same

$$E = C^T H C$$

with lanczos algorithm, one could obtain the result in a matter of seconds.

5.2 Result

$$E = [-2.3028, -1.6180, -1.3028, -1.0000, -0.6180, 0.6180, 1.0000, 1.3028, 1.6180, 2.3028]$$

0.4614	0.0000	-0.3470	0.4082	-0.0000	-0.0000	0.4082	0.3470	0.0000	-0.4614
-0.3006	0.2629	0.3996	-0.0000	-0.4253	0.4253	0.0000	0.3996	0.2629	-0.3006
0.2307	-0.4253	-0.1735	-0.4082	0.2629	0.2629	-0.4082	0.1735	0.4253	-0.2307
-0.2307	0.4253	-0.1735	0.4082	0.2629	-0.2629	-0.4082	-0.1735	0.4253	-0.2307
0.3006	-0.2629	0.3996	-0.0000	-0.4253	-0.4253	0.0000	-0.3996	0.2629	-0.3006
-0.4614	0.0000	-0.3470	-0.4082	-0.0000	-0.0000	0.4082	-0.3470	0.0000	-0.4614
0.3006	0.2629	0.3996	-0.0000	0.4253	0.4253	0.0000	-0.3996	-0.2629	-0.3006
-0.2307	-0.4253	-0.1735	0.4082	-0.2629	0.2629	-0.4082	-0.1735	-0.4253	-0.2307
0.2307	0.4253	-0.1735	-0.4082	-0.2629	-0.2629	-0.4082	0.1735	-0.4253	-0.2307
-0.3006	-0.2629	0.3996	-0.0000	0.4253	-0.4253	0.0000	0.3996	-0.2629	-0.3006

Fig.10 The MO of Naphthalene by column

5.3 Organic Mechanics Explained!

Typical organic chemistry textbooks would reveal that although orientation in the substitution of naphthalene can be complex, the α -position is the most reactive. In this case, the 2,5,7,10th atoms are the α -position, the 3,4,6,9th atoms are the β -position.

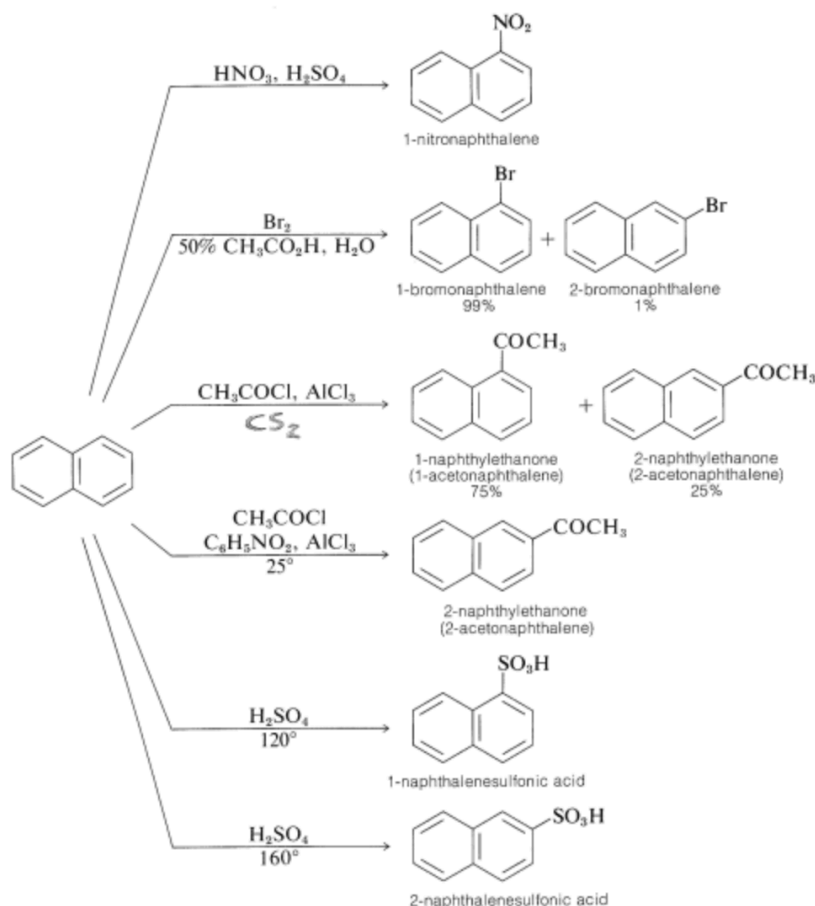


Fig.11 Regional reactivity of Naphthalene. Ignore the fourth and the sixth row, this occurs due to other factors.

With the calculation one proceeded in the previous section, one would easily figure out the exact reason. The π -orbital of the naphthalene molecule contains 10 electrons, which are distributed in the 5 π -orbitals. Among which, the HOMO(Highest Occupied Molecular Orbital) is the reactive one, which according to our calculation, has a wave function like,

$$\psi_6 = 0(\phi_1 + \phi_6) + 0.4253(\phi_2 - \phi_5 + \phi_7 - \phi_{10}) + 0.2629(\phi_3 - \phi_4 + \phi_8 - \phi_9)$$

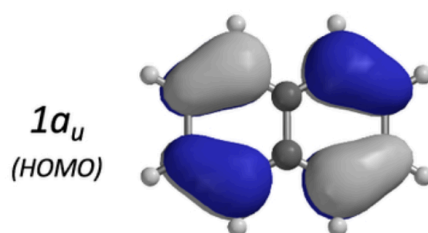


Fig.12 HOMO of Naphthalene

With much of the wave function contributed by the α -position orbital just as other calculation methodologies provided above.

6 Conclusion

In this study, we explored the application of the Hückel method in solving the molecular orbital problem for conjugated systems. We started by introducing the Secular equation and its matrix representation,

which allows us to find the energy levels and coefficients of the linear combination of atomic orbitals that form the molecular orbitals. We then discussed the traditional method of solving the Secular equation using root-finding techniques, such as the multi-section secant method. We also explored the Lanczos algorithm, a linear algebraic method that solves the eigenvalues of the Hamiltonian matrix.

Through our analysis and implementation of these methods, we obtained the orbital energies and wave functions for various conjugated systems, including fulvene and naphthalene. We compared the results obtained from the traditional method and the Lanczos algorithm and found that they were consistent, demonstrating the efficacy of both approaches in solving the molecular orbital problem.

Furthermore, we discussed the significance of the Hückel method in understanding the π -orbital energy order in aromatic compounds. By analyzing the π -orbital energy order, we can gain insights into the stability and reactivity of these compounds. We also highlighted the importance of the Hückel method in simplifying the problem by assuming equal resonance integrals and ignoring the Coulomb integral.

In conclusion, the Hückel method provides a powerful tool for studying the molecular orbital problem in conjugated systems. It allows us to determine the energy levels and wave functions of the molecular orbitals, providing valuable insights into the electronic structure and properties of these systems. The traditional method of solving the Secular equation and the linear algebraic approach using the Lanczos algorithm both yield consistent results, demonstrating the versatility and accuracy of these methods. By applying the Hückel method, we can deepen our understanding of aromatic compounds and their reactivity, paving the way for further advancements in organic chemistry.

Overall, this study highlights the importance of computational methods in solving complex problems in chemistry. The Hückel method, combined with numerical techniques and linear algebra, provides a powerful framework for studying the electronic structure of conjugated systems. Further research can explore the application of these methods to more complex molecules and investigate their potential in other areas of chemistry.



Fig.13 And yes, I know you don't understand a single word of it. Chemistry, folks!