Application of Hückel Theory for Determining MOs and delocalisation energies of some benzenoid compounds and graph theoretical aspects of Hückel theory.

Arghya Modak - 06MS02
Sambit Bikas Pal - 06MS03
Abhishek Dasgupta - 06MS07

Indian Institute of Science Education & Research, Kolkata

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overview

In this work we have used Hückel Theory to determine the MOs of a few members of the homocyclic aromatic class of compounds such as

- Benzene
- Napthalene
- Anthracene
- Tetracene

Hückel theory

Hückel molecular theory..

- introduced by E. Hückel in 1930
- provides the framework for more sophisticated MO treatments
- assumes that the π system of conjugated molecules may be treated independently of the σ bonding

Hückel theory contd....

the approximations

- All overlap integrals are set equal to zero.
- All resonance integrals between non-neighbours are set equal to zero.
- All remaining resonance integrals are set equal to β .

theory

- Using the variational principle we minimise the molecular orbital energy of a conjugated π system.
- We get a system of equations called the secular equations.

$$\begin{aligned}(H_{AA} - E_i S_{AA})\, c_{i,A} + (H_{AB} - E_i S_{AB})\, c_{i,B} &= 0 \\ (H_{BA} - E_i S_{BA})\, c_{i,A} + (H_{BB} - E_i S_{BB})\, c_{i,B} &= 0\end{aligned}$$

$$\mathbf{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \quad \mathbf{S} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \quad \mathbf{c_i} = \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix}$$

In the simple Hückel formulation $\mathbf{S} = \mathbf{I}$ because adjacent overlap integrals are neglected.

So the secular equations expressed in the form of a matrix equation is: **HC = SCE**

By diagonalising the Hückel matrix we get the energy eigenvalues of the molecules. Note that **H** comprises elements H_{ij} where $H_{ii} = \alpha$ which is the energy of the carbon-2p orbital in this case, and all adjacent pairs are β. Thus it naturally follows that **H** can be represented in terms of the adjacency matrix **A** thus:

$$\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A}$$

benzene

The Hückel matrix for benzene is:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

Diagonalising the above we get the following eigenvalues:
$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta$.
From this we see that the delocalisation energy of benzene which is the energy gap between the nonaromatic cyclohexatriene and benzene is 2β. We got β from delocalisation energy of benzene $\rightarrow$ calculated delocalisation energies of the other benzenoid species.

benzene: MOs

$$\begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{pmatrix} = \begin{pmatrix} -1 & -1 & -1 & 1 & -1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 \\ -1 & 1 & 0 & 1 & 0 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 \\ -1 & 0 & 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \\ \psi_5 \\ \psi_6 \end{pmatrix}$$

ϕs are the MOs, ψs are the carbon 2p orbitals.

napthalene

Hückel matrix:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

The eigenvalues obtained were: $x-y, x+y, \frac{1}{2}(2x-y-\sqrt{5}y), \frac{1}{2}(2x+y-\sqrt{5}y), \frac{1}{2}(2x-y+\sqrt{5}y), \frac{1}{2}(2x+y+\sqrt{5}y), \frac{1}{2}(2x-y-\sqrt{13}y), \frac{1}{2}(2x+y-\sqrt{13}y), \frac{1}{2}(2x-y+\sqrt{13}y), \frac{1}{2}(2x+y+\sqrt{13}y)$
delocalisation energy of napthalene: $4\beta \sim 72$ kcal/mol which is quite close to experimental value of 62 kJ/mol

anthracene

Hückel matrix:

$$\begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
\beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\
\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha
\end{pmatrix}$$

The eigenvalues obtained were:

$x-2y, x-y, x-y, x+y, x+y, x+2y, x-\sqrt{2}y, x-\sqrt{2}y, x-y-\sqrt{2}y, x+y-\sqrt{2}y, x+\sqrt{2}y, x+\sqrt{2}y, x-y+\sqrt{2}y, x+y+\sqrt{2}y$

the delocalisation energy of anthracene $= 5.31\beta = 95.57$ kcal/mol which is quite close to experimental value of 84 kcal/mol

tetracene

Hückel matrix:

$$\begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
\beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 & 0 \\
0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\
\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha
\end{pmatrix}$$

18 eigenvalues were obtained (too numerous to list here); however it shows the same pattern as napthalene and anthracene.

other things

Other things we could have found out are:

- electron density $q_\mu = \sum_{j=1} b_j c_{j\mu}^2$.
- bond order $P_{\mu\nu} = \sum_{j=1}^{n} b_j c_{j\mu} c_{j\nu}$

Here b_j is the number of electrons in MO ψ_j, and $c_{j\mu}$ is the coefficient of the MO ψ_j.

heterocyclic stuff

The Hückel formulation can also be applied to heterocyclic molecules such as pyridine. Just a little tweaking to the α and β values is needed:

- α now has an excess term of $h\beta$ over the original Hückel α_{C-C}; so α_{N-N} would be $\alpha_{C-C} + h\beta$.
- β is now written as $k\beta_{C-C}$.

h and k values for C-N systems have been found by Streitweiser, and we have used those values.
h and k depends on number of atoms donated by heteroatom to π-conjugated system. More atoms donated, more should be α; also higher electronegativity $\rightarrow$ less α since α is minus of the ionisation potential (and IP, EN have good +ve correlation)

heterocyclic stuff: pyridine

The Hückel matrix for pyridine is:

$$\begin{pmatrix} (\alpha + h\beta) & k\beta & 0 & 0 & 0 & k\beta \\ k\beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ k\beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

The obtained Eigenvalues are $\alpha + 2.1075\beta, \alpha + 1.167\beta, \alpha + \beta, \alpha - 0.841\beta, \alpha - \beta, \alpha - 1.934\beta$ The delocalisation energy $= 2.00\beta$, same as benzene !

graphs

As we have already seen, the Hückel matrix and the adjacency matrix have a one-one relationship $\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A}$. Studying similarities between various adjacency matrices can help us understand classes of molecules too.

Graph theory has deeper connections with physical chemistry than that which can be gleaned at first sight. We have only skimmed the surface. An example that for alternating hydrocarbons, the energy eigenvalues will be symmetrically distributed about 0. This is known as the *pairing theorem*.

conclusion

In this project, we investigated the Hückel MO theory for determining some parameters of planar aromatic (benzenoid) compounds viz. benzene, napthalene, anthracene and tetracene. In particular we used the one to one relationship between the adjacency matrix and the Hückel matrix to derive the energy eigenvalues of the compounds and from that the **delocalisation energy**. Other things we could have found out are the **electron density** and **bond order**.

There are graph theoretical approaches to study symmetry in molecules and glean useful information from them. Possible future directions in which this project can be extended can be observation of the graph theoretical framework which unites these apparently dissimilar molecules (and predict their properties too).

Thanks!

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