

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

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May 4, 2008

Abstract

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, naphthalene, anthracene and tetracene. A preliminary graph theoretical study was also carried out on these class of molecules to reveal some interesting relationships among them.

Hückel theory

Hückel molecular theory was introduced by E. Hückel in 1930. It provides the framework for more sophisticated MO treatments. This very simple and useful method gives valuable insight into the chemical behaviour of the molecules. It assumes that the π system of conjugated molecules may be treated independently of the σ orbitals and the latter form a rigid framework that determines the general shape of the molecule, thereby greatly simplifying the calculational procedure. Thus the total electronic energy of the molecule can be written as $E = E_{\sigma} + E_{\pi}$ where E_{σ} and E_{π} are respectively the electronic energies arising

due to the σ and π electrons of the molecule. This separation is based on the following argument: A conjugated molecule is in general a planar, or near planar, system. In this very special situation, molecular orbitals or MOs describing the molecule may be partitioned into two orthogonal groups : σ MOs which are symmetric and π MOs which are antisymmetric to reflection in the plane of the molecule. Physically, this approximation may be viewed as one which has π -electrons moving in a potential field due to the nuclei and a σ core, which is assumed to be rigid as the π -electrons move around. All the C atoms are treated identically, so all the Coulomb integrals α for the atomic orbitals that contribute to the π orbitals are set equal.

Hückel theory is based on a number of assumptions known as the Hückel approximations. These are:

1. All overlap integrals are set equal to zero.
2. All resonance integrals between non neighbours are set equal to zero.
3. All remaining resonance integrals are set equal (to β).

These assumptions are obviously very severe but they let us have at least a general picture of the molecular orbital energy levels with very little work. The assumptions result in the following structure of the secular determinant :

1. All diagonal elements : $\alpha - E$.
2. Off-diagonal elements between neighbouring atoms : β .
3. All other elements : 0.

The Hückel theory is based on the **variational principle** which is as follows:

If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy.

Thus according to this principle we first take arbitrary coefficients to construct the wavefunction of the molecule and calculate the energy of the molecule as:

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

Here the appropriate integrals are put equal to α and β . After that we differentiate the expression for the energy with respect to the coefficients and

set them equal to zero. The resulting equations are called the secular equations. It is easy to see that the number of secular equations will be equal to the number of atoms in the molecule as the number of coefficients in the expression will be the same as the number of atoms.

The secular equations are :

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

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

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

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

By diagonalising the Hückel matrix we get the eigenvalues of the molecules. It is to be noted that here

$$H_{rr} = \int \phi_r^* \hat{H} \phi_r d\tau = \alpha$$

and

$$H_{rs} = \int \phi_r^* \hat{H} \phi_s d\tau = \begin{cases} \beta & \text{if } r \text{ and } s \text{ are bonded} \\ 0 & \text{otherwise} \end{cases}$$

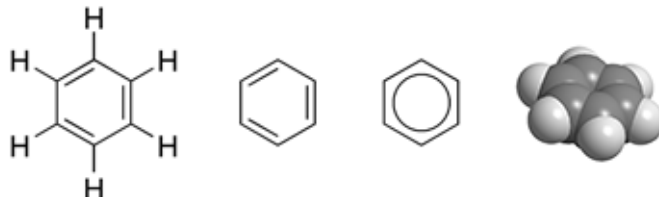
Also

$$S_{rs} = \int \phi_r^* \phi_s d\tau = \begin{cases} 1 & \text{if } r = s \\ 0 & \text{if } r \neq s \end{cases}$$

Thus it naturally follows that \mathbf{H} can be represented in terms of the adjacency matrix \mathbf{A} as $\mathbf{H} = \alpha \mathbf{I} + \beta \mathbf{A}$.

We now come to the calculation for finding out the eigenvalues for the different molecules.

Benzene



For benzene the Hückel matrix is :

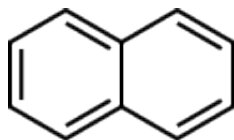
$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

Diagonalising the above matrix we get the following eigenvalues :

$$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta$$

In general the delocalization energy of an aromatic compound is taken to be the energy difference between the compound and its nonaromatic analogue which may be hypothetical. Thus in this case 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 and from there calculated delocalisation energies of the other benzenoid species.

Napthalene



For naphthalene the Hückel matrix is :

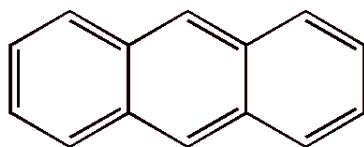
$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0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

The eigenvalues obtained by diagonalizing the above are :

$$x - y, x + y, \frac{1}{2}(2x - y - \sqrt{5}y), \frac{1}{2}(2x + y - \sqrt{5}y), \frac{1}{2}(2x - y + \sqrt{5}y), \frac{1}{2}(2x + y + \sqrt{5}y), \frac{1}{2}(2x - y - \sqrt{13}y), \frac{1}{2}(2x + y - \sqrt{13}y), \frac{1}{2}(2x - y + \sqrt{13}y), \frac{1}{2}(2x + y + \sqrt{13}y)$$

By the procedure followed for benzene and using the value of β got from there the delocalization energy of naphthalene was calculated to be $4\beta \sim 72$ kcal/mol which is quite close to experimental value of 62 kJ/mol .

Anthracene



For anthracene the matrix is :

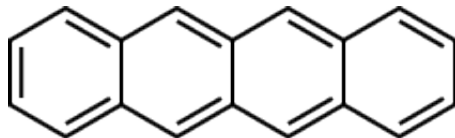
$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 &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

The eigenvalues obtained were :

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

The delocalization energy of anthracene was thus calculated to be $5.31\beta = 95.57$ kcal/mol which is quite close to experimental value of 84 kcal/mol.

Tetracene



For tetracene the matrix is :

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

From here 18 eigenvalues were obtained and the delocalization energy calculated in this case also showed the same pattern.

Other things

For each of the molecules the electron density and the bond order can also be found out by the following equations :

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

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

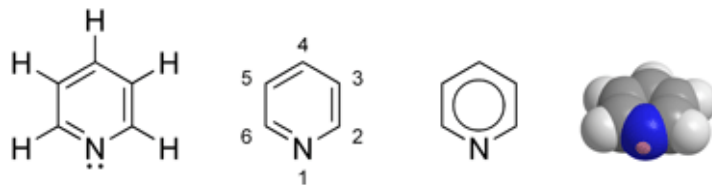
Heterocyclic molecules

The Hückel formulation can also be applied to heterocyclic molecules such as **pyridine**. The main task is to find out the proper numerical values for the Coulomb integral α for the non-carbon atoms and the resonance integral β for bonds other than **C-C** bonds. Proper choice of the Coulomb and resonance integrals are made on some qualitative arguments. For example, since the Coulomb integral represents the negative of the ionization potential, it may be predicted that it should in general follow the electronegativity of the atoms. Thus higher the electronegativity less is the value of α as α is the negative of the ionization energy. Also it depends on the number of electrons donated by the heteroatoms to the π -conjugated system. The more the number of electrons donated higher is the value of α . Thus the following modifications are made :

- 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 those can be used to calculate the eigenvalues for pyridine and other heteronuclear conjugated aromatic molecules with C-N bonds.

Pyridine



Using the same rules as above we construct the Hückel matrix as :

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

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 is 2.00β which is the 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 result follows from graph theory and is known as the *pairing theorem* of Coulson and Rushbrooke.

Conclusion

In this project we investigated the Hückel MO theory for determining some parameters of planar aromatic (benzenoid) compounds viz. benzene, naphthalene, anthracene and tetracene. In particular we used the one to one relationship between the adjacency matrix and the Hückel matrix to derive the energy eigen-

values of the compounds and their **resonance** energies. Other things that could have been calculated are the **electron density** and the **bond order** of these molecules.

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).

Acknowledgement

We are extremely grateful to Prof. B.M. Deb and Prof. S. Bagchi without whose help this project would never have been realised.

References

1. Chemical Graph Theory by Nenad Trinajstić.
2. Electronic Absorption Spectroscopy and Related Techniques by D N Sathyanarayana
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4. All images in this report have been taken from Wikipedia (<http://en.wikipedia.org>).