A4: Theoretical techniques and ideas

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I. RECAP OF HÜCKEL THEORY

We begin with a brief recap of Hückel theory, taking initially the practical viewpoint of 'how-to-do' calculations, rather than the 'meaning' of the subject. We will later return to this latter aspect. This approach, I hope, will have the advantage of getting you started on familiar ground. Actually, Hückel theory is an archetype of more general molecular-orbital theory, and even more widely, of many quantum mechanical principles. Therefore, a good practical grasp of it proves invaluable in many areas of chemistry.

Let us start with the benzene molecule, the Hückel theory of which is very instructive. The steps are as follows. To begin with, we suppose we can treat separately the π-electrons from the σ-electrons. For planar molecules such as benzene, this assumption is strictly justifiable on symmetry grounds, but we will nevertheless assume it to be true for non-planar molecules as well. Next, we set up a "basis" of 6 p_z (or, as we shall sometimes interchangeably refer to them, as p_π) atomic orbitals, one for each carbon in the appropriate geometry. We will label these atomic orbitals $\phi_1, ..., \phi_6$.

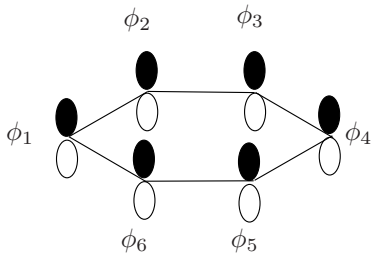


FIG. 1: The p_π atomic orbitals of benzene.

Our aim is to discover the linear combinations of these atomic orbitals which are somehow 'optimal'. To do this, we assume that there is a Hamiltonian operator, $\hat{H}$ (which we will often write simply as H), whose function it is to determine the energy of an electron, and roughly speaking, can be decomposed into three terms: the kinetic energy of the electron, the potential energy of the electron in the nuclear framework, and the potential energy of the electron due

to the average distribution of all other electrons. The precise mathematical form for this effective Hamiltonian it is rather complicated (we will deal with it in C6); for the moment, let us simply assume it exists, with matrix elements:

$$H_{rs} = \langle \phi_r | H | \phi_s \rangle \tag{1}$$

and not concern ourselves with the actual evaluation of these matrix elements (which is generally speaking difficult, and except in a few cases must be done on the computer). One of the beauties of Hückel theory is to assume a simple form for this Hamiltonian - and it turns out that many of the general conclusions of Hückel theory are independent of the actual numerical values of this matrix.

In addition to the Hamiltonian matrix, there is also an *overlap matrix*, which measures the spatial overlap of the orbitals among each other:

$$S_{rs} = \langle \phi_r | \phi_s \rangle \tag{2}$$

If our orbitals are normalised, then $S_{rr} = 1$, and furthermore, if the orbitals are orthogonal to each other, then $S_{rs} = 0$ for $r \neq s$. To begin with, we will not make either assumption.

What we seek are linear combinations of these AO's which are stationary solutions of the Hamiltonian. These special linear combinations are the *molecular orbitals*. We can think of them as standing "waves" whose (square) amplitudes given the probability of finding an electron at that site. Among these waves, for example, is a solution which minimises the energy of the Hamiltonian. We denote an MO with the symbol ψ, and write it as a linear combination of AO's whose coefficients c_r have to be determined:

$$\psi = \sum_r c_r \phi_r \tag{3}$$

Consider the energy of this MO:

$$\epsilon = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{4}$$

Expanding the sum, we get:

$$\epsilon = \frac{\sum_{rs} c_r^* c_s \langle \phi_r | H | \phi_s \rangle}{\sum_{rs} c_r^* c_s \langle \phi_r | \phi_s \rangle} \tag{5}$$

In almost all of the applications we will meet, the coefficients c_r will be real numbers, and it is not necessary to worry about the complex conjugation. In this case, the expression reduces

to:

$$\epsilon = \frac{\sum_{rs} c_r c_s H_{rs}}{\sum_{rs} c_r c_s S_{rs}} \tag{6}$$

Before we continue, let us briefly mention a word about the summation notation. The double sum denoted above means:

$$\sum_{rs} \equiv \sum_{r=1}^{N} \sum_{s=1}^{N} \tag{7}$$

where N is the number of sites in the molecule. Now, it is usually convenient to split the sum up into two parts, terms for which $r = s$ and terms for which $r \neq s$. Thus, assuming a general summand a_{rs}:

$$\sum_{rs} a_{rs} = \sum_{r=1}^{N} a_{rr} + \sum_{r=1}^{N} \sum_{s \neq r}^{N} a_{rs} \tag{8}$$

The third step is that, in all our applications, the summand (a_{rs}) is symmetric:

$$a_{rs} = a_{sr} \tag{9}$$

In this case, the remaining double sum can be further simplified:

$$\sum_{rs} a_{rs} = \sum_{r} a_{rr} + 2 \sum_{r=1}^{N} \sum_{s>r}^{N} a_{rs} \tag{10}$$

$$= \sum_{r} a_{rr} + 2 \sum_{r=1}^{N-1} \sum_{s=r+1}^{N} a_{rs} \tag{11}$$

which we compactly write as:

$$\sum_{rs} a_{rs} = \sum_{r} a_{rr} + 2 \sum_{s>r} a_{rs}. \tag{12}$$

The secular equations

We seek the coefficients c_r such that the energy ϵ is optimised in the sense that the first-derivative wrt c_r all vanish, i.e.

$$\frac{\partial \epsilon}{\partial c_r} = 0 \tag{13}$$

This is a fairly straightforward exercise in partial differentiation with the following fairly simple result. The c_r which satisfy the above are given by the matrix equation:

$$\sum_{r} (H_{sr} - \epsilon S_{sr}) c_r = 0 \tag{14}$$

Written in matrix form we have:

$$\begin{pmatrix} H_{11}-\epsilon S_{11} & H_{12}-\epsilon S_{12} & .... & H_{1N}-\epsilon S_{1N} \\ H_{21}-\epsilon S_{21} & H_{22}-\epsilon S_{22} & .... & H_{2N}-\epsilon S_{2N} \\ .. & .. & .... & ... \\ H_{N1}-\epsilon S_{N1} & H_{N2}-\epsilon S_{N2} & .... & H_{NN}-\epsilon S_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ . \\ c_N \end{pmatrix} = 0 \tag{15}$$

Compactly put, we have:

$$(H-\epsilon S)\mathbf{c} = 0 \tag{16}$$

As you know, the non-trivial solutions to this equation must satisfy:

$$\det(H-\epsilon S) = 0 \tag{17}$$

Or written out in full glory:

$$\begin{vmatrix} H_{11}-\epsilon S_{11} & H_{12}-\epsilon S_{12} & .... & H_{1N}-\epsilon S_{1N} \\ H_{21}-\epsilon S_{21} & H_{22}-\epsilon S_{22} & .... & H_{2N}-\epsilon S_{2N} \\ .. & .. & .... & ... \\ H_{N1}-\epsilon S_{N1} & H_{N2}-\epsilon S_{N2} & .... & H_{NN}-\epsilon S_{NN} \end{vmatrix} = 0 \tag{18}$$

where N is the number of basis functions. It looks awful and we will look for simplifications in a moment. However, there is one general result which we can immediately deduce. Since what we face is an $N \times N$ determinant, should we expand it we would get an N-th order polynomial in ϵ. Since such polynomials have precisely N solutions, we can deduce that there will be N molecular orbitals, or sets of coefficients, $c_r^{(i)}$ which are optimal in the sense of Eq.(13), with associated energies ϵ_i.

So here is the first remarkable result. There are as many sets of solutions c_r as there are functions in your basis! We will label the coefficients as:

$c_r^{(i)}$ where i (the upper label) refers to the MO and r (the lower label) refers to the site.

In nearly everything that we will do in this course, we will assume that the overlap matrix is simply the identity matrix:

$$S_{rs} = \begin{cases} 1 & r = s \\ 0 \text{ otherwise} \end{cases} \tag{19}$$

On the face of it, this assumption is not easily defendable since the overlap between neighbouring p_z orbitals in benzene can be anywhere between 0.25 and 0.4. On the other hand, the effect of including the proper overlap in qualitative terms turns out not to be very significant, and since it simplifies life as regarding the solutions to the problem, we will proceed with it. In this case, the Hückel secular equations substantially simplify:

$$\begin{vmatrix} H_{11}-\epsilon & H_{12} & .... & H_{1N} \\ H_{21} & H_{22}-\epsilon & .... & H_{2N} \\ .. & .. & .... & ... \\ H_{N1} & H_{N2} & .... & H_{NN}-\epsilon \end{vmatrix} = 0 \tag{20}$$

Before we proceed with other simplifications associated with Hückel theory, let us state some properties of the MO's:

$$\text{Orthogonality: } \sum_r (c_r^{(i)})^* c_r^{(j)} = 0 \text{ for } i \neq j. \tag{21}$$

[Note the complex conjugation in the above. It will usually have no effect because we normally work with real orbitals. On occasion, complex orbitals do arise, particularly in ring systems, and then you to have to take care]. In addition, it is strongly recommended that you *always* work with normalised orbitals:

$$\text{Normalisation: } \sum_r |c_r^{(i)}|^2 = 1 \tag{22}$$

This condition ensures that the probability to find your electron *somewhere* on one of the N sites must be unity [why?]. Having computed MO's according to some method you should check to see if each one is indeed normalised. If not, then the coefficients should be replaced by:

$$c_r^{(i)} \rightarrow \frac{c_r^{(i)}}{(\sum_r |c_r^{(i)}|^2)^{1/2}} \tag{23}$$

Normalisation will be essential for computing a number of properties later on, such as bond-orders, atomic populations, etc. In a normalised MO ψ_i, with orthogonal AOs, the probability to find an electron on site r is:

$$p_r^{(i)} = |c_r^{(i)}|^2 \tag{24}$$

The Hückel assumptions

Now let us proceed by making certain assumptions which simplify actual calculations.

- We set all diagonal elements to be the same: $H_{ii} = \alpha$, irrespective of where the ϕ_i occurs in the molecule. Clearly for benzene and other rings this is strictly true (not an approximation), whereas in general it is not. We will later discuss what actual numerical values α could be assigned (you will see experiment is not clear-cut on this issue). Roughly speaking α measures the energy of the AO ϕ in the complete framework of the molecule. It is often (somewhat misleadingly) called the Coulomb integral, which is not correct since it also contains kinetic energy terms. In the limit of the molecule being torn apart into its consitutent atoms, it is the energy of a p orbital. Note, however, that in the molecule, it is not simply this energy, since the orbital also sees the field due to the other nuclei (and electrons).

- We also set the off-diagonal elements between nearest-neighbour orbitals to be β, and all others to be zero:

$$H_{rs} = \begin{cases} \beta & r \to s, \text{ i.e. if } \sigma\text{-bonded to each other} \\ 0 & \text{otherwise} \end{cases} \tag{25}$$

Thus, at the end of all this we have, for benzene, the following 'secular' determinant to solve:

$$\begin{vmatrix} \alpha-\epsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-\epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-\epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-\epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-\epsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-\epsilon \end{vmatrix} = 0 \tag{26}$$

You can see that we've eliminated a lot of elements, but we still appear to face a somewhat daunting task of solving a 6×6 determinant. Actually we will see in another lecture how this (and more generally, cyclic polyenes, and also linear chains) can be easily solved using some nifty algebra, but for the moment we will appeal to another method which is more general and which you've already had plenty of exposure at Part IB: using symmetry.

II. USING SYMMETRY TO SIMPLIFY THE SOLUTION OF HÜCKEL PROBLEMS

The point-group of the benzene molecule is D_{6h}, and you will from last year's experience immediately be able to work out the irreducible representations spanned by the six p_z orbitals:

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_{p_z}	6	0	0	0	−2	0	0	0	0	−6	0	2

(27)

which can be reduced to

$$\Gamma_{p_z} = B_{2g} + E_{1g} + A_{2u} + E_{2u} \tag{28}$$

This means that we can setup 4 classes of symmetry adapted orbitals (which correspond to 4 irreducible representations of the D_{6h} point group), 2 one-dimensional irreps (B_{2g} and A_{2u}) and 2 two-dimensional irreps (E_{1g} and E_{2u}). In this basis (which we will shortly setup), the Hamiltonian is in block-diagonal form:

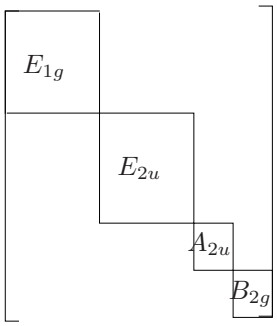
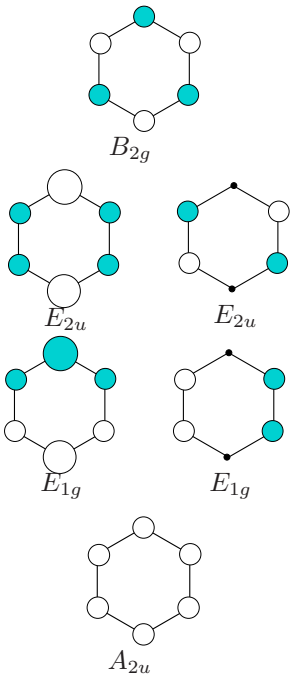


FIG. 2: Block diagonal form of the benzene Hamiltonian

By inspection of character tables (or, more formally, using the projector operator), we can write down the symmetry adapted orbitals:

$$\begin{aligned}
\phi_{A_{2u}} &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \\
\phi_{B_{2g}} &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\
\phi^{(1)}_{E_{2u}} &= \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \\
\phi^{(2)}_{E_{2u}} &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \\
\phi^{(1)}_{E_{1g}} &= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) \\
\phi^{(2)}_{E_{1g}} &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)
\end{aligned}$$



Note that these orbitals are orthonormal to each other, i.e. the scalar product between any pair vanishes, whilst the norm of each orbital is unity. (Indeed the orthonormality condition is a useful device to construct the second of a pair of orbitals in a 2d irrep such as E_{2u} and E_{1g}). Since the 1d irreps A_{2u} and B_{2g} do not mix with other orbitals, and in this case they are singletons, these symmetry-adapted orbitals are already also the molecular orbitals. Their energy can be written down by inspection, using Eq.(6):

$$\psi_{A_{2u}} = \phi_{A_{2u}}, \quad \epsilon_{A_{2u}} = \langle \psi_{A_{2u}} | H | \psi_{A_{2u}} \rangle = \alpha + 2\beta \tag{29}$$

$$\psi_{B_{2g}} = \phi_{B_{2g}}, \quad \epsilon_{B_{2g}} = \langle \psi_{B_{2g}} | H | \psi_{B_{2g}} \rangle = \alpha - 2\beta \tag{30}$$

For the E_{2u} block, we can set up the 2×2 matrix by evaluating the matrix elements $\langle \phi^{(i)}_{E_{2u}} | H | \phi^{(j)}_{E_{2u}} \rangle$

$$H_{E_{2u}} = \begin{pmatrix} \alpha - \beta & 0 \\ 0 & \alpha - \beta \end{pmatrix} \tag{31}$$

which is already diagonal, and leads to the two energy eigenvalues:

$$\psi^{(1)}_{E_{2u}} = \phi^{(1)}_{E_{2u}}, \quad \psi^{(2)}_{E_{2u}} = \phi^{(2)}_{E_{2u}}, \quad \epsilon_{E_{2u}} = \alpha - \beta \quad \text{(2-fold degenerate)} \tag{32}$$

and similarly for the E_{1g} block:

$$\psi^{(1)}_{E_{1g}} = \phi^{(1)}_{E_{1g}}, \quad \psi^{(2)}_{E_{1g}} = \phi^{(2)}_{E_{1g}}, \quad \epsilon_{E_{1g}} = \alpha + \beta \quad \text{(2-fold degenerate)} \tag{33}$$

Irrep	ϵ_i	c_1	c_2	c_3	c_4	c_5	c_6	Normalisation	Nodes
A_{2u}	$\alpha+2\beta$	1	1	1	1	1	1	$\frac{1}{\sqrt{6}}$	0
E_{1g}	$\alpha+\beta$	2	1	-1	-2	-1	1	$\frac{1}{\sqrt{12}}$	2
E_{1g}	$\alpha+\beta$	0	1	1	0	-1	-1	$\frac{1}{2}$	2
E_{2u}	$\alpha-\beta$	2	-1	-1	2	-1	-1	$\frac{1}{\sqrt{12}}$	4
E_{2u}	$\alpha-\beta$	0	1	-1	0	-1	1	$\frac{1}{2}$	4
B_{2g}	$\alpha-2\beta$	1	-1	1	-1	1	-1	$\frac{1}{\sqrt{6}}$	6

Table I: Molecular orbitals of benzene

The results are summarised below in table I.

Given six π-electrons, which doubly occupy the three lowest energy levels, the total π-energy is:

$$E_\pi = 6\alpha + 8\beta \tag{34}$$

leading to a delocalisation energy of:

$$\begin{aligned} E_{delocalisation} &= E_\pi - 3\times 2(\alpha+\beta) \\ &= 2\beta \end{aligned}$$

which is the amount the aromatic system is stabilised compared to a system of 3 isolated π-bonds, which is what the corresponding Kekulé structure would lead one to predict.

Compared to hexatriene, the linear counterpart to benzene, the delocalisation energy of benzene is much larger in magnitude. In fact, for hexatriene, one finds [Verify!]

$$\begin{aligned} E_{delocalisation} &= 4\beta\left[\cos(\pi/7)+\cos(2\pi/7)+\cos(3\pi/7)\right]-6\beta \\ &\approx 0.99\beta \end{aligned}$$

In other words, the ring structure greatly stabilises the π-energy. Indeed this can be taken as a rationalisation of the fact that aromatic systems tend to be stable, and undergo substitution reactions, whereas linear chains tend to undergo addition reactions.

III. WHAT OF VALUES FOR β AND α?

Although we have stressed that many of the conclusions of Hückel theory are independent of the numerical values of α and β (this is particularly true of the α parameter), it is nev-

ertheless interesting to ask what type of experimental result could be used to yield values. One idea is to use experimental delocalisation energies, which are tabulated for the series benzene, naphthalene, anthracene and phenanthrene (the "zig-zag" form of anthracene):

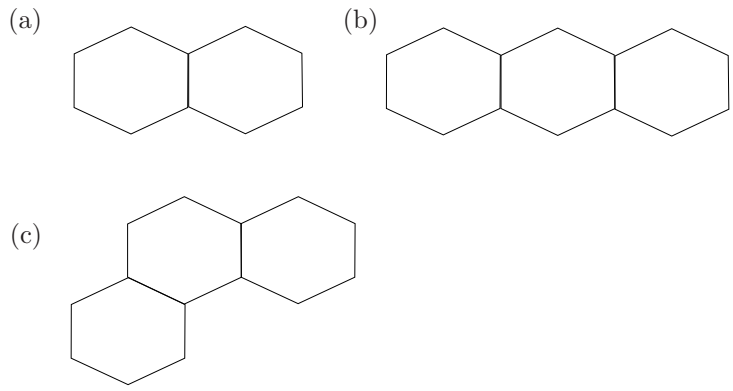


FIG. 3: (a) Naphthalene, (b) Anthracene and (c)Phenanthrene

Two conclusions can be drawn from this. First, the close parallel between the Hückel the-

Molecule	Theory	Experiment	Estimate of β
Benzene	2β	37 (kcal/mol)	18.5 (kcal/mol)
Naphthalene	3.68β	75 (kcal/mol)	20.4 (kcal/mol)
Anthracene	5.32β	105 (kcal/mol)	19.7 (kcal/mol)
Phenanthrene	5.45β	110 (kcal/mol)	20.2 (kcal/mol)

Table II: Delocalisation energies.

ory prediction on the variation of the delocalisation energy for the series, as compared to experiment, which indicates that even such crude calculations are able to reproduce a significant trend. Taking β to be about -20 kcal/mol leads to a reasonable agreement between predicted and experimental delocalisation energies; thus naphthalene is about twice as additionally stable compared to the Kekulé structures, as is benzene, and anthracene is about three times as stable, etc. The second point regards the difference between anthracene and phenanthrene, the latter being slightly more stable. Indeed, this trend continues for larger systems: the annulation to give "zig-zag" forms are indeed experimentally more stable then the corresponding linear ones (eg chrysene is more stable than tetracene). Thus our very crude theory is able to give some interesting, semi-quantitative, results.

Matters look less rosy if we consider a different type of measurement of β, using ionisation potentials. Recall that the first ionisation potential is the minimum energy required to remove an electron from a molecule, and therefore it is reasonable to suppose that the electron removed comes from HOMO. Since, according to Hückel theory, the energy of an orbital can be written in the form:

$$\epsilon = \alpha + x\beta$$

where x is suitable coefficient which depends on the molecule, one may suppose that if we take a series of molecules (eg benzene, naphthalene, anthracene, etc), for which the x can be calculated, and plot the ionisation energy as a function of x, then the slope of such a (hopefully linear) curve would yield β, whereas the intercept would yield α. It turns out that a least-squares fit yields:

$$\text{Experimental ionisation energy} = -163 + (-57 \pm 3.9)x \text{ kcal/mol} \tag{35}$$

i.e. a value of $\beta \approx -57$ kcal/mol, which is more than twice that value obtained from the delocalisation energies. In fact this turns out to be a quite general feature of Hückel theory. Experiments which depend on the energy of *single* orbitals turn out to yield values of β which are always roughly a factor of two larger that those bases on *total* energies, in which the energies of many orbitals are summed together.

The explanation for this behaviour can be found by considering the manner in which electron-electron interactions are dealt with in the Hamiltonian H. Recall that the H is an effective Hamiltonian in which an electron sees the average field due to all other electrons. In other words, electron 1 sees a field due to the average of electrons 2, 3 , etc, and this field, in addition to the field due to the nuclear framework, determines the energy eigenvalue of electron 1. Similarly, electron 2 sees the average field of electron 1, electron 3, etc, and its energy eigenvalue reflects these interactions as well. Therefore, if we add the energy eigenvalue of electron 1 and electron 2, we have *counted twice* the average electrostatic interaction between electron 1 and electron 2. This is exactly what is done in our method of calculating the total π-energy: we simply add the energy of all occupied levels. On the other hand, if we are dealing with purely the energy of a single energy level, there is no double counting. Therefore, it should not be surprising that methods used to estimate β based on the total energies yield values about 1/2 of that from ionisation potential experiments.

IV. SOME SPECIAL SYSTEMS: LINEAR CHAINS AND RINGS OF ARBITRARY LENGTH

In two general cases, it is possible to solve the Hückel equations to get the energy levels and molecular orbital coefficients with little ado. Consider first a cyclic polyene (ring) of N atomic sites. In such a ring, site r is connected to sites $r+1$ and $r-1$, with the boundary

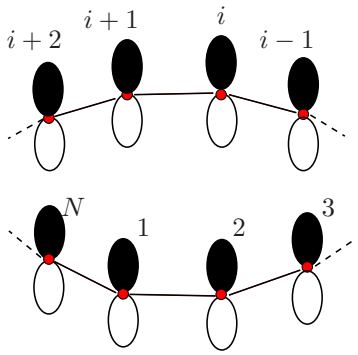


FIG. 4: A cyclic polyene of length N

condition

$$c_r^{(n)} = c_{N+r}^{(n)}. \tag{36}$$

In the above, n signifies the molecular orbital label. A row in the Hückel equations is:

$$(\alpha - \epsilon_n)c_r^{(n)} + \beta(c_{r+1}^{(n)} + c_{r-1}^{(n)}) = 0 \tag{37}$$

Let us guess the following solution:

$$c_r^{(n)} = e^{i2\pi nr/N} \tag{38}$$

(which, you should note, satisfies the boundary condition Eq.(36)), and insert into Eq.(37):

$$(\alpha - \epsilon_n)e^{i2\pi nr/N} + \beta(e^{i2\pi n(r+1)/N} + e^{i2\pi n(r-1)/N}) \;=\; 0 \tag{39}$$

Notice that one can factorise $e^{i2\pi nr/N}$ and hence cancel this term, leaving an equation which no longer involves the site r:

$$(\alpha - \epsilon_n) + \beta(e^{i2\pi n/N} + e^{-i2\pi n)/N}) \;=\; 0 \tag{40}$$

i.e.:

$$\epsilon_n = \alpha + 2\beta\cos(2\pi n/N) \tag{41}$$

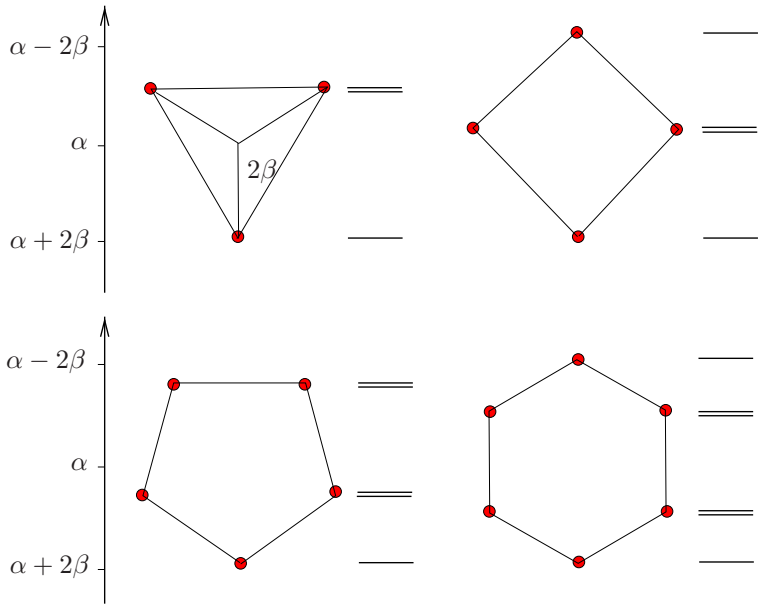


FIG. 5: The energy levels of the first few cyclic polyenes.

where n runs from $0, \pm 1, \pm 2..., N/2$ for even-N or $n = 0, \pm 1, \pm 2, ..., \pm(N-1)/2$ for odd-N. There are always precisely N MO's. Since the $\cos(x)$ is an even function, this implies that, apart from $n = 0$ and $n = N/2$, the energy levels come in degenerate pairs. The energy levels for the first few cyclic polyenes are be represented in Fig. 5.

This structure of the energy levels of the cyclic polyenes has an interesting consequence, leading to the Hückel $4N + 2$ rule. Consider the sequence of cyclic polyenes with $N = 3$ to 7:

C_3H_3: In the neutral molecule, there are 3 π-electrons. However, owing to the energy level pattern, the third electron occupies an anti-bonding orbital. Therefore, one would expect that the cation $C_3H_3^+$ to be more stable than the neutral species, and therefore that it should be easy to remove an electron from the molecule.

C_4H_4. In this molecule, there are a two degenerate non-bonding orbitals, which in the neutral species are partially occupied. According to Hund's first rule, the expected electronic configuration is a triplet state. However, this is the case to be expected only if the molecule is indeed *square* planar. In fact a distortion of the molecular geometry can occur. As a result, cyclobutadiene takes on a rectangular structure, in which the bonds alternate in length, (long-short-long-short).

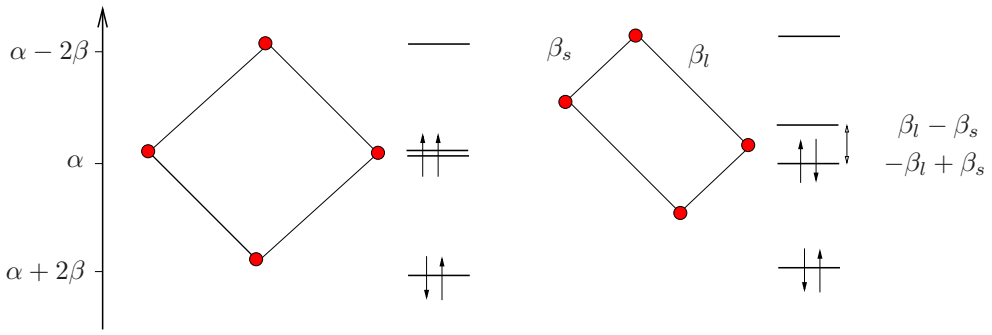


FIG. 6: Distortion of the cyclobutadiene leads to two different β, and a consequent lifting of degeneracy of the partially filled orbitals, which lowers the electronic energy.

A conjugated system with such alternating bond-lengths is characterised by two resonance integrals $|\beta_l| < |\beta_s|$. In this case, the secular equations give rise to a different energy level pattern. The degenerate non-bonding orbitals are lifted, and as a result, the lowering of energy leads to a double occupancy of the HOMO, and hence a singlet state. Such a geometric distortion leading to this effect is called a pseudo-Jahn-Teller or Renner distortion.

C_5H_5: In neutral cyclopentadiene, the highest occupied energy level (2-fold degenerate) is a bonding orbital ($\epsilon_1 = \alpha + 0.618\beta$) and is partially occupied with 3 electrons. These levels are therefore able to accept a further electron with a consequent stabilisation. One would expect, therefore, that the anion $C_5H_5^-$ to exist, consisting of 6 π electrons.

C_6H_6. This case, benzene, has already been dealt with. All bonding orbitals are occupied in the neutral molecule, and there are no non-bonding orbitals.

C_7H_7. In the neutral molecule, the highest occupied MO is an anti-bonding orbital, and therefore this molecule can be expected to have a tendency to shed an electron, forming a cation.

On the basis of these observations, would you expect the following molecule, azulene, to exhibit a significant dipole moment, and if so, in which direction?

In order to obtain normalised MO's, one must have:

$$\sum_r (c_r^{(n)})^* c_r^{(n)} = 1 \tag{42}$$

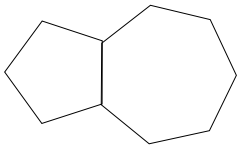


FIG. 7: Azulene

Since, for Eq.(38),

$$(c_r^{(n)})^* c_r^{(n)} = e^{-i2\pi nr/N} e^{i2\pi nr/N} = 1, \tag{43}$$

we have:

$$c_r^{(n)} = \frac{1}{\sqrt{N}} e^{i2\pi nr/N} \tag{44}$$

A mathematical aside: Notice that for degenerate pairs, the coefficients in Eq.(44) appear different to those computed earlier for benzene, Eq.(32) and Eq.(33) for the E_{2u} and E_{1g} states. Note, however, that in the latter representation, the coefficients of the orbitals can be expressed as:

$$E_{2u} \ : \ c_r^{(1)} = \cos(2\pi r/6), \quad c_r^{(2)} = \sin(2\pi r/6) \tag{45}$$

$$E_{1g} \ : \ c_r^{(1)} = \cos(4\pi r/6), \quad c_r^{(2)} = \sin(4\pi r/6) \tag{46}$$

These coefficients are simply linear transformations of those in Eq.(44), via:

$$\frac{1}{2}(e^{i2\pi nr/6} + e^{-i2\pi nr/6}) \ = \ \cos(2\pi nr/6), \tag{47}$$

$$\frac{1}{2i}(e^{i2\pi nr/6} - e^{-i2\pi nr/6}) \ = \ \sin(2\pi nr/6) \tag{48}$$

Thus an alternative, purely real, representation of the orbitals of the cyclic polyenes are:

$$c_r^{(n)} \ = \ C_n \cos(2\pi nr/N), n = 0, 1, 2..., (N-1)/2 \quad (N \text{ odd }) or N/2 \quad (N \text{ even}) \tag{49}$$

$$s_r^{(n)} \ = \ S_n \sin(2\pi nr/N), n = 1, 2, ..., (N-1)/2 \quad (N \text{ odd }) or N/2 \quad (N \text{ even}) \tag{50}$$

C_n and S_n are normalisation factors which, unlike Eq.(44), must be computed separately for each MO. Note also that for N even, the solution arising from $N/2$ is identical for both the sine and cosine expressions, and should therefore only be counted once.

A. Linear polyene chains

A similar trick can be applied to the linear chain of N sites. In this case, we impose the boundary conditions that the wavefunction must vanish beyond either end of the molecule,

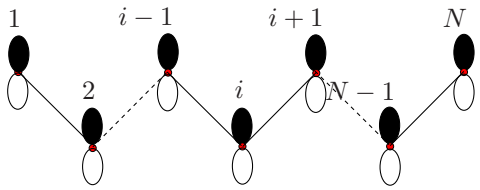


FIG. 8: A linear polyene of length N

i.e. if the atomic sites are labelled 1,...,N, we set the coefficient of all molecular orbitals "off-the-end" of the molecule to zero:

$$c_0^{(n)} = c_{N+1}^{(n)} = 0 \tag{51}$$

The Hückel equations Eq.(37) must now be solved with these boundary conditions. Let us guess the following solution:

$$c_r^{(n)} = \sin(n\pi r/(N+1)) \tag{52}$$

which satisfies the boundary conditions Eq.(51). Substitution into Eq.(37) gives:

$$(\alpha - \epsilon_n)\sin(n\pi r/(N+1)) + \beta(\sin(n\pi(r+1)/(N+1)) + \sin(n\pi(r-1)/(N+1))) \;=\; 0$$

Using:

$$\sin(a \pm b) = \sin(a)\cos(b) \mp \cos(a)\sin(b)$$

we obtain:

$$\begin{aligned}(\alpha - \epsilon_n)\sin(n\pi r/(N+1)) \;+\; & \beta(\sin(n\pi r/(N+1))\cos(\pi n/(N+1)) \\ & +\; \sin(n\pi r/(N+1))\cos(\pi n/(N+1))) = 0\end{aligned}$$

and hence:

$$(\alpha - \epsilon_n) + 2\beta(\cos(\pi n/(N+1))) \;=\; 0$$

i.e.

$$\epsilon_n = \alpha + 2\beta\cos(\pi n/(N+1)) \tag{53}$$

which is similar but not the same as the energy-level expression for the cyclic polyenes: The linear chain does not have the doubly-degenerate levels characteristic of the cyclic system.

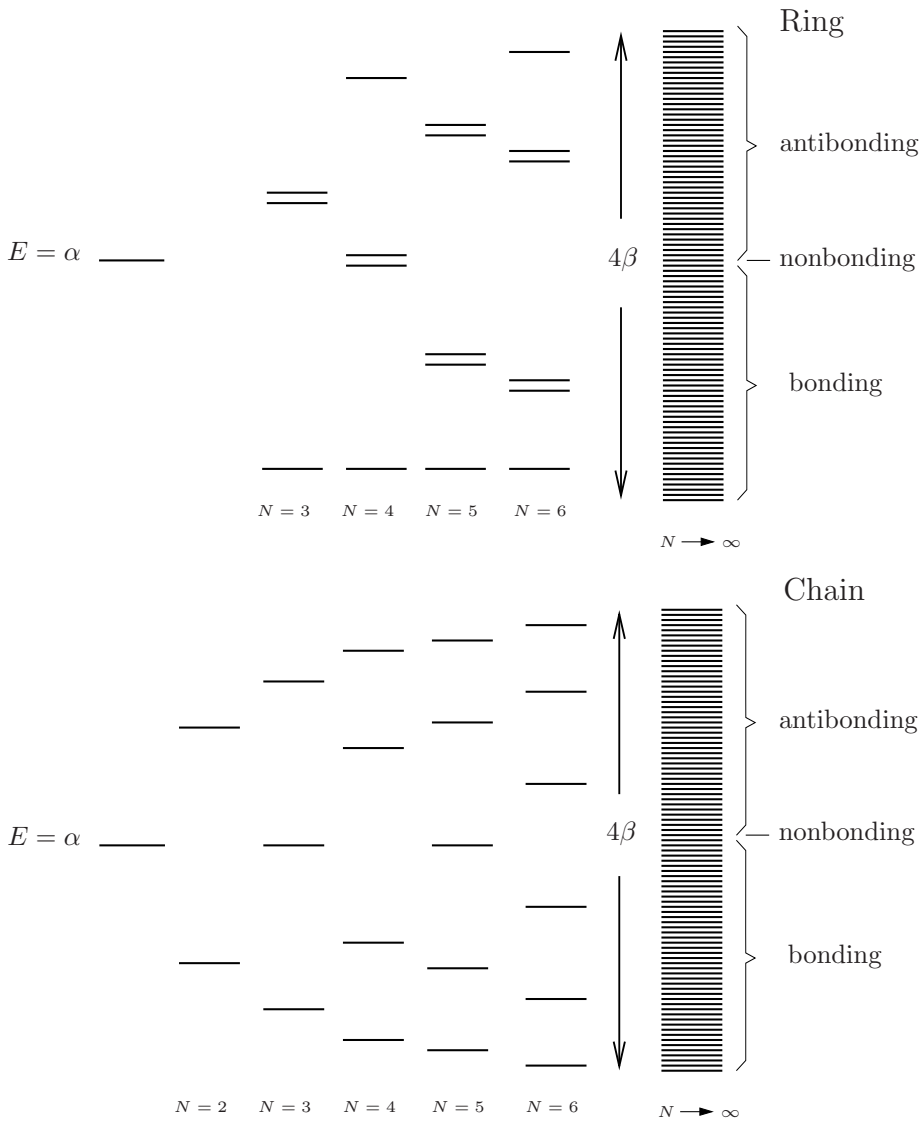


FIG. 9: Comparison of the energy levels of cyclic and linear polyenes.

In addition, whereas the rings all have a deep bonding (and high anti-bonding) level at the lowest (highest) possible energy $\mp 2\beta$, the width of the linear chain band grows and reaches 4β only in the limit of an infinitely long chain.

Normalisation of the linear-chain coefficients leads to:

$$c_r^{(n)} = \sqrt{\frac{2}{N+1}} \sin(n\pi r/(N+1)) \tag{54}$$