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 $\phi_1, ..., \phi_6$.
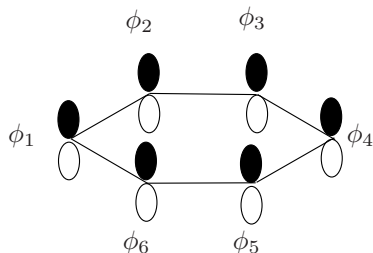

FIG. 1: The p_π atomic orbitals of benzene.

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:

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

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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:

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

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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:

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

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:

$$
\begin{array}{c|cccccccccccc}
D_{6h} & E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \\
\hline
\Gamma_{p_z} & 6 & 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & -6 & 0 & 2
\end{array}
\tag{27}
$$

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:
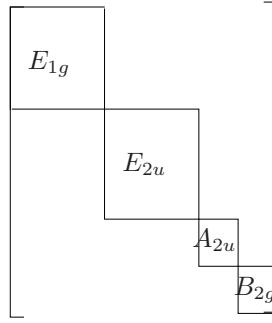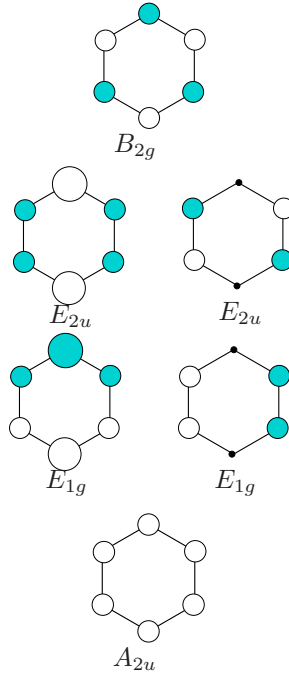

FIG. 2: Block diagonal form of the benzene Hamiltonian

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

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

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 $\langle \phi_{E_{2u}}^{(i)} | H | \phi_{E_{2u}}^{(j)} \rangle$

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

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

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

and similarly for the E_{1g} block:

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

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):
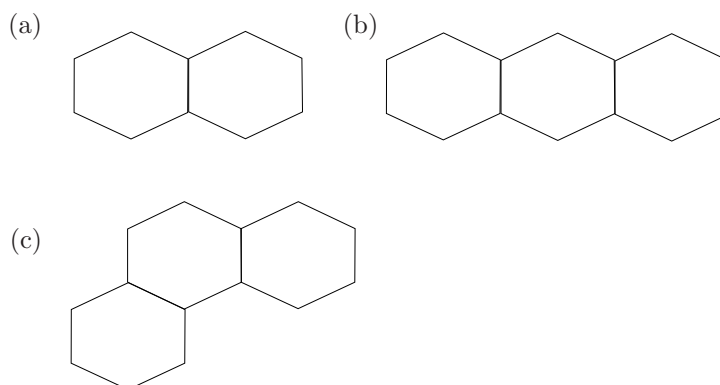

FIG. 3: (a) Naphthalene, (b) Anthracene and (c)Phenanthrene

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.

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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
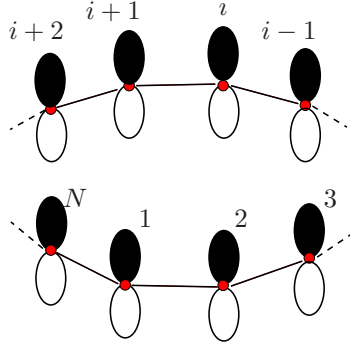

FIG. 4: A cyclic polyene of length N

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:

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

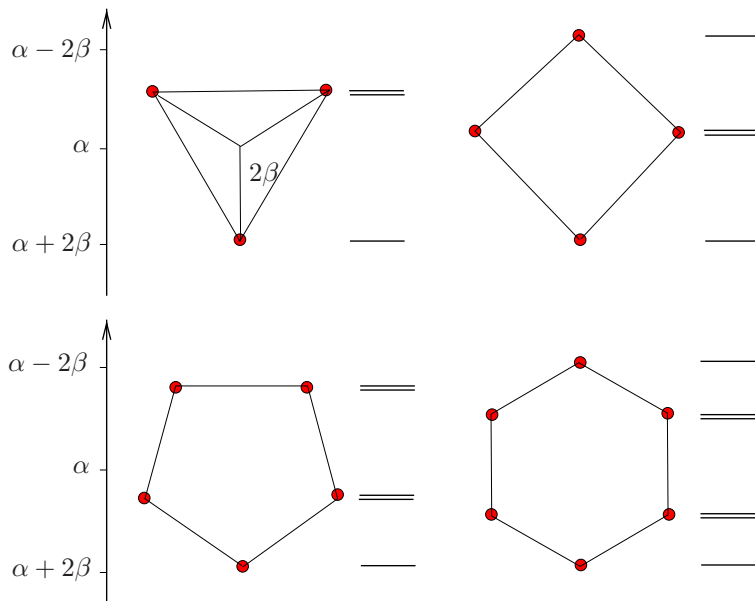i.e.:

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

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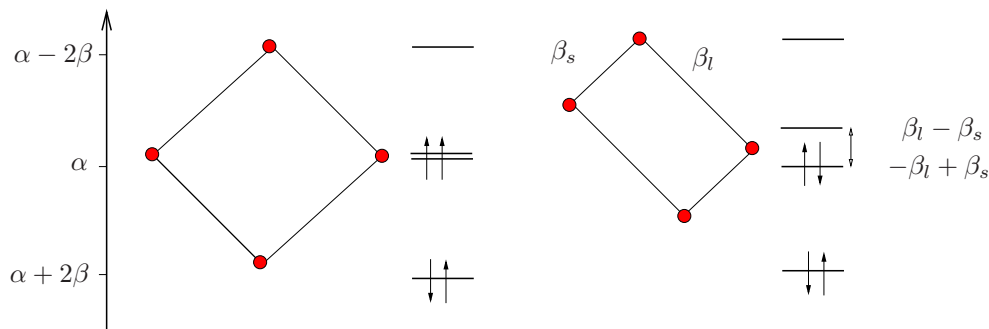
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FIG. 6: Distortion of the cyclobutadiene leads to two different β, and a consequent lifting of degeneracy of the partially filled orbitals, which lowers the electronic energy.

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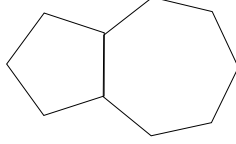
$$\sum_r (c_r^{(n)})^* c_r^{(n)} = 1 \tag{42}$$

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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,
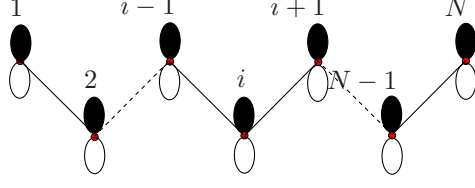
15

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:

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

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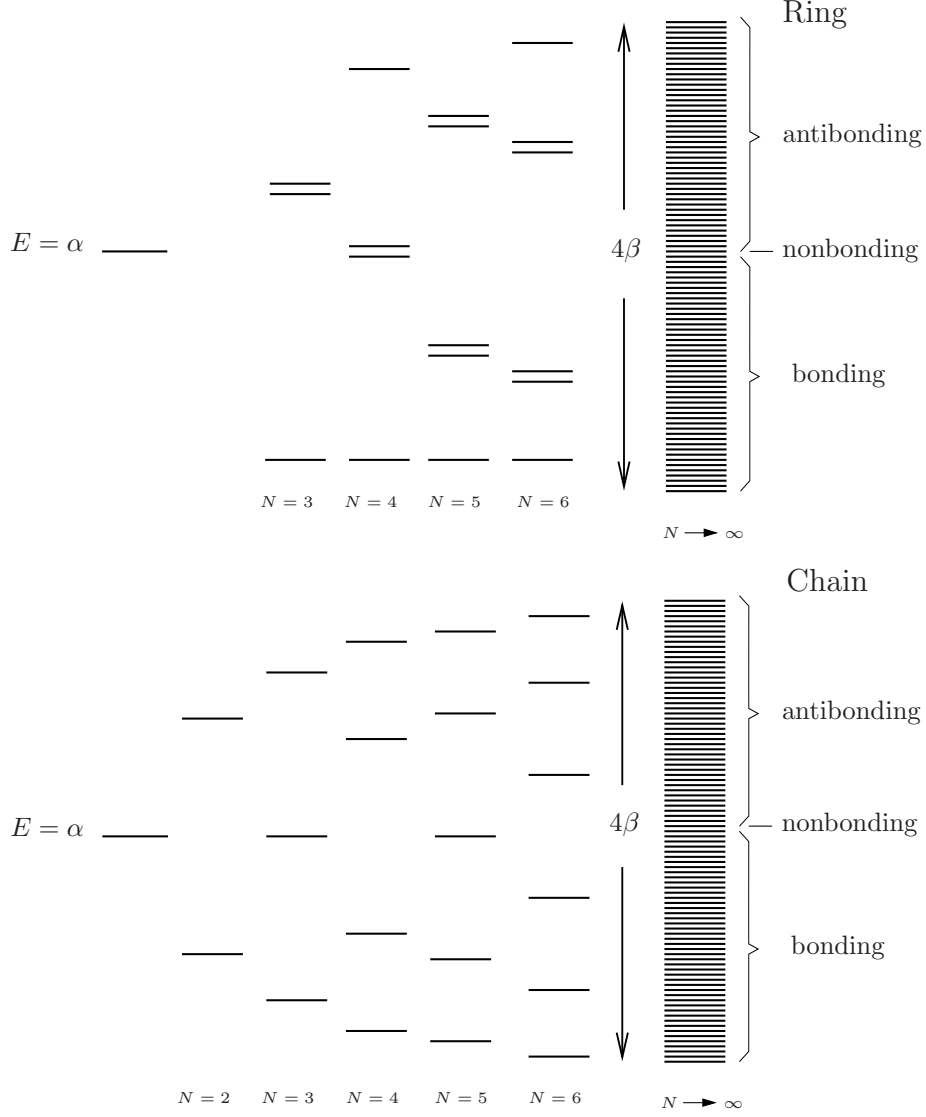
FIG. 9: Comparison of the energy levels of cyclic and linear polyenes.

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:

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

V. POPULATIONS AND BOND ORDERS

The solutions to the Hückel equations yield molecular orbitals, which are typically delocalised over the entire molecule. One might ask about the typical electronic charge on a given site as a result of populating certain MO's, and to ask if there is a measure of the bonding/anti-bonding interaction between a pair of atoms.

A reasonable definition of the total π-electron population at atomic site r is:

$$q_r = \sum_i f_i |c_r^{(i)}|^2 \tag{55}$$

where the sum runs over the orbitals, f_i is the occupation of the orbital, i.e. 2,1, or 0, for doubly, singly and unoccupied levels, and $c_r^{(i)}$ is the coefficient of the ith orbital (normalised of course) on the rth site. This expression is using that fact that, in MO i, the π-electron density at site r is $|c_r^{(i)}|^2$. [Take care, if using complex orbitals, to use the square-magnitude of the orbital, *not* simply its square].

If the MOs are all either doubly occupied, or empty, (which is case for closed-shell molecules), then the expression for the populations reduces to:

$$q_r = 2 \sum_{i \in occ} |c_r^{(i)}|^2 \qquad \text{(Closed shell molecules)} \tag{56}$$

where the notation $i \in occ$ implies that you sum only over the occupied MOs.

A bond order between two atomic sites, r, s can be analogously defined by:

$$p_{rs} = \left(\sum_i f_i \frac{1}{2} \left[(c_r^{(i)})^* c_s^{(i)} + \underbrace{c_r^{(i)} (c_s^{(i)})^*}_{complex conjugate} \right] \right) \tag{57}$$

$$= \sum_i f_i c_r^{(i)} c_s^{(i)} \qquad \text{for real orbitals} \tag{58}$$

The rationale for this is that $c_r^{(i)} c_s^{(i)}$ can be thought of as a "bonding charge" in MO i between sites r and s, which can be positive (accumulation), negative (depletion) or zero.

As for populations, for closed-shell molecules the bond-order has a simpler form:

$$p_{rs} = 2 \sum_{i \in occ} c_r^{(i)} c_s^{(i)} \qquad \text{(closed shell molecule with real orbitals)} \tag{59}$$

As a first example, let us compute the populations and bond orders in benzene. In this case, since all atomic sites are equivalent, we need compute the population for one site only. Taking site 1, and using the MOs in Table I:

$$q_1 = 2 \left[\frac{1}{6} + \frac{4}{12} + 0 \right] = 1$$

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You should explicitly verify that the charges on the other sites are likewise equal to one. Note also that the use of the complex version of the MOs would have given you the same result:

$$q_1 = \frac{1}{6}\left(1 \times 2 + e^{i2\pi/6}e^{-i2\pi/6} \times 2 + e^{i4\pi/6}e^{-i4\pi/6} \times 2\right) = 1$$

For the bond orders we obtain:

$$
\begin{aligned}
p_{12} &= 2\left[\frac{1}{6} + \frac{2}{\sqrt{12}} \times \frac{1}{\sqrt{12}}\right] \\
&= \frac{2}{3}
\end{aligned}
$$

In other words, in benzene, each atomic site has the same electron density residing on it, and a π-bond-order of $2/3$ between nearest neighbour sites.

Let us next consider the linear analogue of benzene, hexatriene. In this case, the occupied normalised molecular orbitals are:

$$c_r^{(n)} = \sqrt{\frac{2}{7}}\sin(n\pi r/7) \tag{60}$$

with $n = 1, 2, 3$. We find:

$$q_1 = q_6 = \frac{2 \times 2}{7}\left(\sin^2(\pi/7) + \sin^2(2\pi/7) + \sin^2(3\pi/7)\right) = 1$$

You should show for yourselves that the remaining charges are also all unity (this is less obvious):

$$q_2 = q_5 = q_3 = q_4 = 1$$

In other words, the π-electron populations on the linear chain are equal, irrespective of the position of the carbon atom along the chain. The bond-orders, however, show a variation:

$$
\begin{aligned}
p_{12} &= \frac{2 \times 2}{7}\left(\sin(\pi/7)\sin(2\pi/7) + \sin(2\pi/7)\sin(4\pi/7) + \sin(3\pi/7)\sin(6\pi/7)\right) = 0.871 \\
p_{23} &= \frac{2 \times 2}{7}\left(\sin(2\pi/7)\sin(3\pi/7) + \sin(4\pi/7)\sin(6\pi/7) + \sin(3\pi/7)\sin(6\pi/7)\right) = 0.484 \\
p_{34} &= TODO!
\end{aligned}
$$

i.e the two bond-orders at the end-molecule are almost twice that the neighbouring bond, confirming our intuition of an alternating pattern of single and double bonds. Note also that, the outer bonds are stronger - and the central bonds weaker - than the corresponding bond-orders in benzene.

VI.   ALTERNANT HYDROCARBONS

One of the most useful general applications of Hückel theory is to rationalise the differing properties of "alternant" and "nonalternant" hydrocarbons". An alternant hydrocarbon is one in which the carbon atoms can be divided into a "starred" class, and a "non-starred" class, such that each starred atom is neighboured only by an unstarred atom, and vice versa. Two examples in Fig. 10 illustrate this.

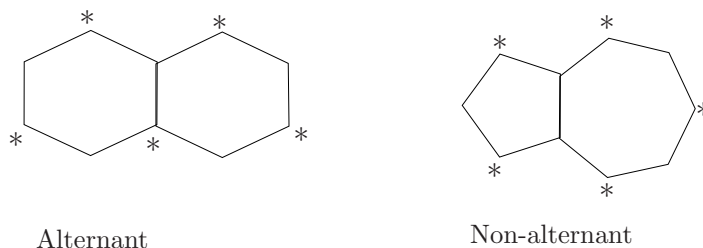Alternant   Non-alternant

FIG. 10: Examples of successful and unsuccessful starring processes

With a little thought you should be able to convince yourself that, *for a hydrocarbon to be alternant, it should not possess an odd-membered ring*. Therefore, all linear-chain hydrocarbons, as are molecules consisting of fused benziod rings (e.g. naphthalene,anthracene, etc) are alternant, whereas odd(n) annulenes such as azulene are non-alternant.

Alternant hydrocarbons have the following properties in Hückel theory (which can be fairly easily proven):

(1) The energy levels of alternant hydrocarbons are symmetrically paired about an appropriate zero (α), such that if $\epsilon_i = \alpha + k\beta$ is a root of the secular equation, then so is $\epsilon_{N-i+1} = \alpha - k\beta$. This type of pattern in the energy levels is evident in Fig. 5.

An implication of this theorem is that an odd-alternant hydrocarbon must possess a nonbonding orbital (with energy $\epsilon = \alpha$).

(2)In an alternant hydrocarbon, the coefficients in the AO expansion of the MO's, any pair of complementary orbitals (ie. $\alpha + k\beta$ and $\alpha - k\beta$) are identical, apart from a change in the sign of the coefficients of the AO's centred on the unstarred atoms.

(3) In any neutral alternant (which can be a radical), the atomic populations in the ground-state are precisely unity. This is quite a surprising result since it holds even in situations are the atomic sites are inequivalent - we have seen an example of this in the linear hexatriene system. It also implies that in a molecule like naphthalene, the π charges are equally distributed around the molecule.

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Proofs of some or all of these statements may be provided during the lectures. Otherwise they should be considered as most interesting exercises.

A very useful device in alternant hydrocarbon theory concerns the non-bonding MO which occurs in odd-alternants. The coefficients of the AOs in such an MO can be easily calculated. One can show [exercise] that coefficients of the smaller set (usually called the unstarred set) are zero, and that the sum of the coefficients of its neighbouring AO's is also zero.
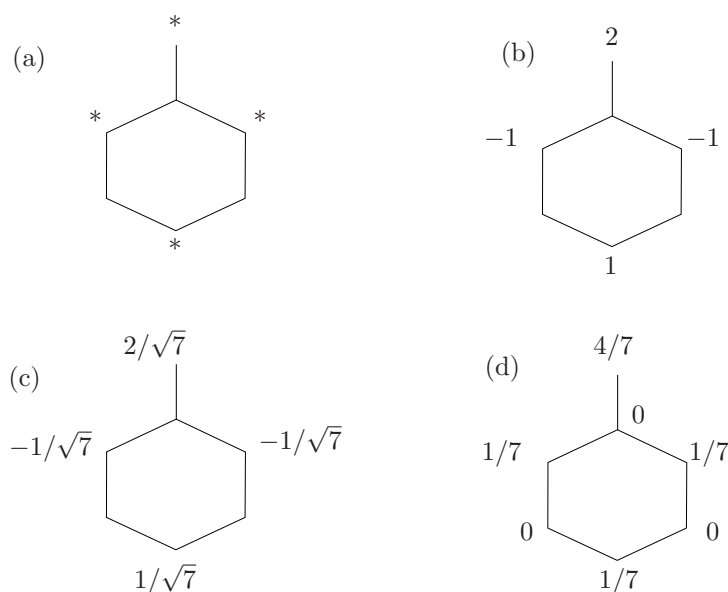
For example, consider the benzyl radical:

FIG. 11: (a) Starring in the benzyl radical,. (b) Un-normalised AO coefficients. (c) Normalised AO coefficients. (d) π-electron density.

This procedure shows that the non-bonding, radical, electron has a maximum in density on the terminal carbon atom (being 4 times as likely as at the ortho or para positions), whilst having no density at all on the meta positions. This observation in fact forms the basis of a "law of alternating polarity", since electron density is more likely to flow from the positions in which the non-bonding electron density is high. This effect will be observed in hetero-conjugated systems.

VII. HETEROCONJUGUATED SYSTEMS

If in a π-system we substitute a carbon atom for, say, nitrogen, then a simple Hückel theory can be devised to taken this into account, by allowing to change the α and β parameter

associated with that site.

The α parameter for atom r, which is related to the Hamiltonian via $\alpha_r = \langle \phi_r | H | \phi_r \rangle$, can be regarded as a measure of the electron-attracting ability of an atom, i.e. it is related to the electronegativity of the atom in question. It is conventional to express the difference in α for an atom r and compared to that of carbon in units of β (taking β between two neighbouring carbon-atoms as the standard), i.e. $\beta \equiv \beta_{CC}$, to write:

$$\alpha_r - \alpha_C = h\beta, \text{ or } \alpha_r = \alpha_C + h\beta$$

The value of h is the defining parameter, which must be chosen with regard to the nature of the substituent. For example, consider pyridine and pyrrole:

FIG. 12: The π system of pyridine and pyrrole

The N atom in pyridine is sp^2 hybridised, with two of the hybrid orbitals forming σ bonds with the neighbouring C atoms, and the third hybrid forming a lone pair. This leaves one electron, which is donated into the π-network. In pyrrole, however, the N is also sp^2 hybridised, but this time the presence of an H bonded to the N means that the N can donate 2 electrons into the π-network.

As an example, let us solve for Hückel equations for pyridine, taking $\alpha_N = \alpha + 1.5\beta$, and

$\beta_{NC} = 0.8\beta$. The Hückel secular determinant is a 6×6 matrix:

$$\begin{vmatrix} \alpha_N - \epsilon & \beta_{NC} & 0 & 0 & 0 & \beta_{NC} \\ \beta_{NC} & \alpha - \epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - \epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - \epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - \epsilon & \beta \\ \beta_{NC} & 0 & 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0$$

As before, by appealing to symmetry we can simplify the problem somewhat. The point group is C_{2v}. From "descent in symmetry" tables, we can see that in going from $D_{6h} \to C_{2v}$,

$$A_{2u} \to B_2$$
$$B_{2g} \to B_2$$
$$E_{2u} \to A_2 + B_2$$
$$E_{1g} \to A_2 + B_2$$

Therefore, we should expect to be able to reduce the 6×6 pyridine Hückel Hamiltonian into a $4 \times 4(B_2)$ and $2 \times 2(A_2)$ matrices. Let us see how this arises.

The p_z orbitals (ϕ_2, ϕ_6) transform into each other and thereby form a 2d representation, as do (ϕ_3, ϕ_5), whilst ϕ_3 and ϕ_N each form 1d-representations. From group theory tables we can easily deduce the irreps spanned:

$$\Gamma_N = B_2$$
$$\Gamma_{2,6} = B_2 + A_2$$
$$\Gamma_{3,5} = B_2 + A_2$$
$$\Gamma_4 = B_2$$

Therefore, we can reduce the problem to a 4×4 matrix (B_2) and a 2×2 matrix (A_2). Constructing the symmetry orbitals of the B_2 problem:

$$\phi_{B_2}^{(1)} = \frac{1}{\sqrt{2}}(\phi_2 + \phi_6)$$
$$\phi_{B_2}^{(2)} = \frac{1}{\sqrt{2}}(\phi_3 + \phi_5)$$

Thus the Hückel secular determinant for this irrep becomes:

$$
\begin{vmatrix}
\alpha_N - \epsilon & \sqrt{2}\beta_{NC} & 0 & 0 \\
\sqrt{2}\beta_{NC} & \alpha - \epsilon & \beta & 0 \\
0 & \beta & \alpha - \epsilon & \sqrt{2}\beta \\
0 & 0 & \sqrt{2}\beta & \alpha - \epsilon
\end{vmatrix} = 0
$$

Substituting the chosen values of $\alpha_N = \alpha + \frac{1}{2}\beta$ and $\beta_{NC} = 0.8\beta$, and letting $x = (\alpha - \epsilon)/\beta$, we obtain:

$$
\begin{vmatrix}
x - \frac{1}{2} & 0.8\sqrt{2} & 0 & 0 \\
0.8\sqrt{2} & x & 1 & 0 \\
0 & 1 & x & \sqrt{2} \\
0 & 0 & \sqrt{2} & x
\end{vmatrix} = 0
$$

This is as far as one can go using symmetry. The solution to the quartic polynomial is done numerically, to obtain two bonding, and two anti-bonding, orbitals:

$$
B_2 : \epsilon_1 = \alpha + 1.954\beta
$$

$$
\epsilon_2 = \alpha + 1.062\beta,
$$

$$
\epsilon_3 = \alpha - 0.667\beta,
$$

$$
\epsilon_4 = \alpha - 1.845\beta
$$

For the A_2 block, we have the following symmetry orbitals:

$$
\phi_{A_2}^{(1)} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_6)
$$

$$
\phi_{A_2}^{(2)} = \frac{1}{\sqrt{2}}(\phi_3 - \phi_5)
$$

leading to the matrix:

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

giving two unperturbed orbitals:

$$
A_2 : \epsilon_5 = \alpha + \beta
$$

$$
\epsilon_6 = \alpha - \beta
$$

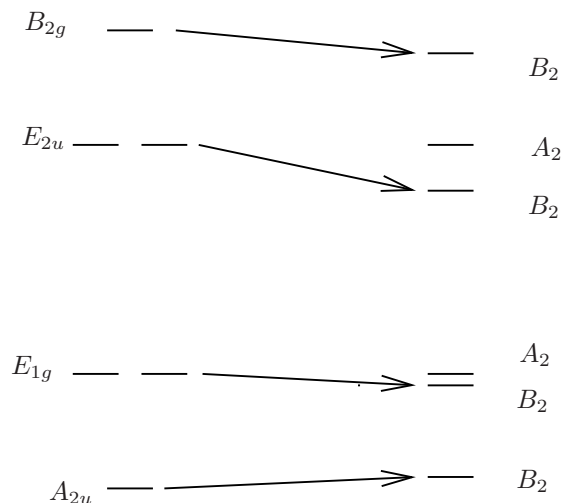The energy levels are represented in Fig. 13

FIG. 13: π energy levels of benzene and pyridine

The comparison with benzene is instructive.

For reference, the coefficients of the MOs are given in Table III. You should verify or derive these for yourself.

ϵ_i	c_N	c_2	c_3	c_4	c_5	c_6
$\alpha + 1.954\beta$	0.424	0.386	0.414	0.424	0.414	0.386
$\alpha + 1.062\beta$	0.665	0.234	-0.284	-0.535	-0.284	0.234
$\alpha + \beta$	0	-0.5	-0.5	0	0.5	0.5
$\alpha - 0.667\beta$	-0.564	0.412	0.177	-0.530	0.177	0.412
$\alpha - \beta$	0	-0.5	0.5	0	-0.5	0.5
$\alpha - 1.845\beta$	0.243	-0.357	0.465	-0.503	0.465	-0.357

Table III: Molecular-orbital coefficients of pyridine

These can be used to compute the atomic populations and bond-orders (see exercise).

The overall energy of the molecule is:

$$E_{pyridine} = 2 \times (\epsilon_1 + \epsilon_2 + \epsilon_3) = 6\alpha + 8.032\beta$$

implying

$$\Delta E = 0.032\beta \tag{61}$$

We shall shortly develop an approximate, but much easier method, to compute approximately the energy levels and eigenstates of hetero-conjugated systems based on perturbation theory.

It is also of considerable interest to compute the π-electron density for pyridine, using the MOs computed above. We find (verify) for pyridine, as well as its cation and anion, the following populations:
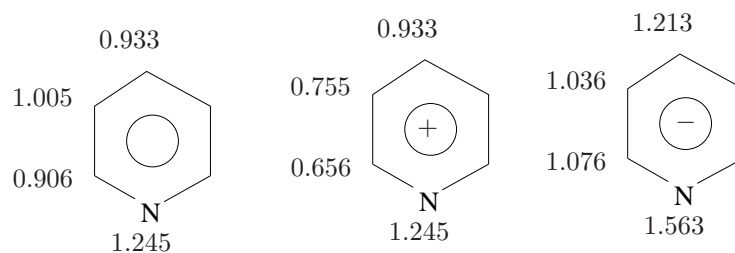

FIG. 14: Site populations on pyridine, and its cation and anion

Such calculations begin to throw light on where nucleophilic or electrophilic attack is likely to occur in pyridine, and from the charge distribution of the cation and anion, when removing (or adding) an electron, which site loses (or gains) the most. Such simple calculations are very insightful in discussing a whole range of chemical properties such as reactivity.

VIII. PERTURBATION THEORY

The concept of a "perturbation", or more precisely a "perturbing Hamiltonian", is simple and is well illustrated by the heteroatom problem. The pyridine molecule Hückel Hamiltonian can be written as the original benzene Hückel matrix, plus a another matrix, which is the

perturbation:

$$H_{pryidine} = \begin{pmatrix} \alpha_N & \beta_{NC} & 0 & 0 & 0 & \beta_{NC} \\ \beta_{NC} & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta_{NC} & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

$$= \underbrace{\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}}_{H_{benzene}} + \underbrace{\begin{pmatrix} \frac{\beta}{2} & -0.2\beta & 0 & 0 & 0 & -0.2\beta \\ -0.2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -0.2\beta & 0 & 0 & 0 & 0 & 0 \end{pmatrix}}_{U} \tag{62}$$

(where we have assumed $\alpha_N = \alpha + \beta/2$ and $\beta_{NC} = 0.8\beta$). You see that in the present case, the perturbing matrix has non-zero elements only along the first row and column, which results from the fact only one site, namely the N, was changed.

More generally, suppose we are given a Hamiltonian H, which we can divide into two parts, $H^{(0)}$ and U, where $H^{(0)}$ is the reference Hamiltonian whose energy levels and MO's we have already calculated, and U is the perturbation:

$$H = H^{(0)} + U \tag{63}$$

One can ask the question: assuming the perturbing Hamiltonian is "small", how can one express, even if only approximately, the energy levels and MOs of the perturbed Hamiltonian (e.g. $H_{pyridine}$) in terms of the unperturbed one, (e.g. $H_{benzene}$)?

Actually this is a very general and important topic which forms a entire lecture course in itself (B7). Perturbation theory has an extraordinary number of applications. We will not have the time to dwell into it in great detail, but will present the main results, and not derive them in any rigorous way.

Change in energy levels

If the energy level ϵ_i is non-degenerate and the corresponding MO is given by ψ_i, then the (first-order) change in energy induced by the perturbation is:

$$\Delta\epsilon_i^{(1)} = \langle\psi_i|U|\psi_i\rangle \tag{64}$$

In terms of the coefficients $c_r^{(i)}$ of the MO this is:

$$
\begin{aligned}
\Delta\epsilon_i^{(1)} &= \sum_r |c_r^{(i)}|^2 U_{rr} + \sum_{r\neq s}(c_r^{(i)})^* c_s^{(i)} U_{rs} \\
&= \sum_r |c_r^{(i)}|^2 U_{rr} + \sum_{r>s}(c_r^{(i)})^* c_s^{(i)} U_{rs} + c_r^{(i)}(c_s^{(i)})^*(U_{sr})^* \\
&= \sum_r |c_r^{(i)}|^2 U_{rr} + 2\sum_{r>s} c_r^{(i)} c_s^{(i)} U_{rs} \quad \text{[For real orbitals]}
\end{aligned}
\tag{65}
$$

For degenerate levels (eg the E_{1g} and E_{2u} levels of benzene), *the same formula holds as long as you have checked that the off-diagonal matrix elements of the perturbing Hamiltonian are zero.* In other words, if ψ_i and ψ_j are a degenerate pair, then as long as

$$\langle\psi_i|U|\psi_j\rangle = 0 \tag{66}$$

the first order change in energy is given by Eq.(65). If the degenerate pair do not satisfy this condition, then it is necessary to do something more complicated. More on this later.

As an example, let us consider the pyridine molecule, taking benzene to be the unperturbed molecule. First, consider the lowest energy level:

$$\psi_1 = \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right)$$

i.e. the coefficients are $c_r^{(1)} = 1/\sqrt{6}$ for all sites. The energy of this state is $\epsilon_1 = \alpha + 2\beta$.

According to Eq.(65), the first-order change energy in going from benzene to pyridine is:

$$\Delta\epsilon_1^{(1)} = \langle\psi_1|U|\psi_1\rangle = \frac{1}{6}\left(\frac{\beta}{2} - 0.2\beta \times 2 \times 2\right) = -0.05\beta$$

Therefore, the energy of this state is:

$$\epsilon_1 \approx \alpha + 1.95\beta, \quad [EXACT\, \epsilon_1 = \alpha + 1.954\beta]$$

The error compared to the exact value is only approximately 0.2%.

Consider next the degenerate pair

$$\psi_2 = \frac{1}{\sqrt{12}}\left(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6\right)$$

$$\psi_3 = \frac{1}{2}\left(\phi_2 + \phi_3 - \phi_5 - \phi_6\right)$$

Now, for the combination above, you can verify that:

$$\langle\psi_2|U|\psi_3\rangle = 0$$

Therefore, we can proceed directly to compute the first order change in energy:

$$\Delta\epsilon_2^{(1)} = \frac{1}{12}\left(4 \times \frac{\beta}{2} + 2 \times 2 \times (-0.2\beta) \times 2\right) = 0.033\beta$$

$$\Delta\epsilon_3^{(1)} = 0$$

i.e.:

$$\epsilon_2 \approx \alpha + 1.033\beta, \quad [EXACT = \alpha + 1.062\beta]$$

$$\epsilon_3 = \alpha + \beta, \quad [EXACT = \alpha + \beta] \tag{67}$$

In other words, the lowering of the B_2 level is underestimated, whilst its originally degenerate partner is left unperturbed (exact).

The total change of energy predicted by first-order perturbation theory is:

$$\Delta E^{(1)} = (-0.05 \times 2 + 0.033 \times 2)\beta = -0.033\beta \tag{68}$$

which is not very accurate, since it implies that the energy of pyridine has increased (more positive), whereas the exact result shows a decrease of 0.032. This inaccuracy can be traced to the above-noted underestimation of the perturbation of the E_{1g} level. For better accuracy, one needs higher-order perturbation theory. Fortunately, the comparison between the total energies of benzene and pyridine tends not be so important, and so this lack of accuracy does not detract from the usefulness of even 1st order perturbation theory.

If the degenerate pair of levels which are being perturbed do not satisfy the condition: $U_{12} = \langle\psi_1|U|\psi_2\rangle = 0$, then one needs to solve the following secular equation for the first-order change $\Delta\epsilon^{(1)}$:

$$\begin{vmatrix} U_{11} - \Delta\epsilon^{(1)} & U_{12} \\ U_{21} & U_{22} - \Delta\epsilon^{(1)} \end{vmatrix} = 0$$

which gives a quadratic equation in $\Delta\epsilon^{(1)}$. Notice that if $U_{12} = 0$, then the first order change are given by:

$$\Delta\epsilon_1^{(1)} = U_{11}, \qquad \Delta\epsilon_2^{(1)} = U_{22}$$

which is the result already stated. You should repeat the above exercise, using the complex degenerate pair:

$$\psi_2(r) = \frac{1}{\sqrt{6}}e^{i2\pi r/6}, \text{and } \psi_3(r) = \frac{1}{\sqrt{6}}e^{-i2\pi r/6}$$

and satisfy yourselves that this procedure gives the same result as Eq.(67).

Changes in the molecular orbitals

To compute the first-order changes in the MO's, perturbation theory gives the following formula for the change in ψ_i:

$$\Delta\psi_i^{(1)} = \sum_j{}' \frac{\langle\psi_j|U|\psi_i\rangle}{\epsilon_i - \epsilon_j}\psi_j \tag{69}$$

where

$$\langle\psi_j|U|\psi_i\rangle = \sum_r c_r^{(i)}c_r^{(j)}U_{rr} + \sum_{r>s}(c_r^{(i)}c_s^{(j)} + c_s^{(i)}c_r^{(j)})U_{rs} \tag{70}$$

The sum over j in Eq.(69) runs over *all* MO's (occupied and unoccupied), except for i (that is the meaning of the $'$). Again, this formula holds only for non-degenerate states. It is clear that for degenerate states, the denominator vanishes and Eq.(69) cannot work. For degenerate states, the same procedure carried out for the energy-levels must be performed, i.e. one must ensure that the matrix elements $\langle\psi_i|U|\psi_j\rangle = 0$ by working with the appropriate linear combinations of the degenerate set $\{\psi_i, \psi_j, ...,\}$.

Use of this formula implies quite a lot of work, since to compute the change for each MO, one has to evaluate matrix elements, and then summations, over all other MO's. Notice, however, that the important contributions to the perturbed MO occur when the denominator $\epsilon_i - \epsilon_j$ is small and when the numerator $\langle\psi_i|U|\psi_j\rangle$ is large. The first condition implies that widely separated in energy levels will not mix in significantly

Let us see how this works for pyridine, taking benzene as its reference. First, we compute the matrix elements $\langle\psi_i|U|\psi_j\rangle$. For example, taking $\psi_1 = (1/\sqrt{6})(1, 1, 1, 1, 1, 1)$ and $\psi_2 =$

$(1/\sqrt{12})(2, 1, -1, -2, -1, 1)$, we have:

$$\langle \psi_1 | U | \psi_2 \rangle = \frac{1}{\sqrt{6 \times 12}} \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \frac{\beta}{2} & -0.2\beta & 0 & 0 & 0 & -0.2\beta \\ -0.2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -0.2\beta & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 \\ 1 \\ -1 \\ -2 \\ -1 \\ 1 \end{pmatrix}$$

$$= \frac{1}{\sqrt{6 \times 12}} (\beta/2 \times 2 + 6 \times (-0.2\beta)) = -0.024\beta \tag{71}$$

Similarly, for the other matrix elements we find (verify):

$$\langle \psi_1 | U | \psi_3 \rangle = 0$$

$$\langle \psi_1 | U | \psi_4 \rangle = 0.071\beta$$

$$\langle \psi_1 | U | \psi_5 \rangle = 0$$

$$\langle \psi_1 | U | \psi_6 \rangle = 0.083\beta$$

Therefore, the first-order change in ψ_1 is:

$$\Delta^{(1)}\psi_1 = \frac{-0.024\beta}{(\alpha + 2\beta) - (\alpha + \beta)}\psi_2 + \frac{0.071\beta}{3\beta}\psi_4 + \frac{0.083\beta}{4\beta}\psi_6$$
$$= -0.024\psi_2 + 0.024\psi_4 + 0.021\psi_6$$

Expressed in terms of atomic orbitals, we have:

$$\Delta^{(1)}\psi_1 = 0.0085(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

Looking at the coefficient, we see an increase in amplitude at the N atom, and the next nearest C atoms, whilst amplitude has drained away from the neighbouring C atoms and the one diametrically opposite.

Carrying out the similar analysis for ψ_2 we find (do as exercise):

$$\Delta^{(1)}\psi_2 = \frac{-0.024\beta}{(-\beta)}\psi_1 + \frac{0.167\beta}{2\beta}\psi_4 + \frac{0.165\beta}{3\beta}\psi_6$$
$$= 0.024\psi_1 + 0.084\psi_4 + 0.055\psi_6$$
$$= 0.022(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

Bearing in mind that the unperturbed level was:

$$\psi_2 = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

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we see that the amplitude on N has further increased, and also on C atom 4. Thus the expected changes in charge density are increases on N, decreases on the two neighbouring C's, and smaller changes on more distant C atoms. This is as observed in the exactly computed π populations, Fig. 14.

Changes in populations and bond orders

With the above results in hand, we can now work now the changes in the π electron density, q_r, induced by a perturbation. Consider, first, a change in a single α parameter on site s: $\alpha_s \to \alpha + \delta\alpha_s$. How does this affect q_r, i.e. the population at site r? For simplicity, we will do the analysis assuming real orbitals. Since:

$$q_r = \sum_i f_i (c_r^{(i)})^2 \tag{72}$$

we have:

$$\frac{\partial q_r}{\partial \alpha_s} = \sum_i f_i \times 2c_r^{(i)} \times \frac{\partial c_r^{(i)}}{\partial \alpha_s} \tag{73}$$

Since the perturbation occurs on a single site, the perturbation Hamiltonian is very simple, and we have:

$$\begin{aligned}
\frac{\partial c_r^{(i)}}{\partial \alpha_s} &= \sum_j{}' \frac{(\partial U/\partial \alpha_s)_{ji}}{\epsilon_i - \epsilon_j} c_r^{(j)} \\
&= \sum_j{}' \frac{c_s^{(i)} c_s^{(j)}}{\epsilon_i - \epsilon_j} c_r^{(j)}
\end{aligned} \tag{74}$$

Substituting into the above, we arrive at:

$$\frac{\partial q_r}{\partial \alpha_s} = 2 \sum_i \sum_{j \neq i} f_i \times \frac{c_r^{(i)} c_s^{(i)} c_s^{(j)} c_r^{(j)}}{\epsilon_i - \epsilon_j} \tag{75}$$

Noting that the summand is antisymmetric wrt interchange of i and j, this implies that summation of the index j over *occupied* states cancels precisely the terms over i (which are, due to the presence of the f_i only over occupied states), leaving:

$$\frac{\partial q_r}{\partial \alpha_s} = 4 \sum_{i \in occ} \sum_{j \in unocc} \frac{c_r^{(i)} c_s^{(i)} c_s^{(j)} c_r^{(j)}}{\epsilon_i - \epsilon_j} \tag{76}$$

We will find an application for this formula shortly. Let us note an important aspect about its structure. In general the principal contributions to it come from the HOMO and LUMO

states, since in this case the denominator is smallest. In many cases, one can draw qualitatively correct conclusions by focusing exclusively on the 'action' at the HOMO and LUMO.

In the literature, you will sometimes come across the term "self-polarisability" and "mutual polarisability", which describe the diagonal and off-diagonal elements, and are denoted by π_r and π_{rs} respectively:

$$\pi_r = \frac{\partial q_r}{\partial \alpha_r}, \tag{77}$$

$$\pi_{rs} = \frac{\partial q_r}{\partial \alpha_s} \tag{78}$$

As an example, let us calculate the change in the π electron density on the N atom in pyridine induced by a change $\Delta\alpha_N = \beta/2$ using this formula. Here we have (it is helpful to consult Table I at this point!):

$$
\begin{aligned}
\frac{\partial q_N}{\partial \alpha_N} &= 4 \sum_{i=1}^{3} \sum_{j=4}^{6} \frac{c_N^{(i)} c_N^{(i)} c_N^{(j)} c_N^{(j)}}{\epsilon_i - \epsilon_j} \\
&= 4 \left[\frac{1}{6} \left(\underbrace{\frac{4}{12 \times 3\beta}}_{i=1,j=4} + \underbrace{\frac{1}{6 \times 4\beta}}_{i=1,j=6} \right) + \frac{4}{12} \left(\underbrace{\frac{4}{12 \times 2\beta}}_{i=2,j=4} + \underbrace{\frac{1}{6 \times 3\beta}}_{i=2,j=6} \right) \right] \\
&= 4 \left[\frac{1}{54\beta} + \frac{1}{144\beta} + \frac{1}{18\beta} + \frac{1}{54\beta} \right] \\
&= \frac{0.40}{\beta} \tag{79}
\end{aligned}
$$

Overall, therefore:

$$
\begin{aligned}
\Delta q_N &\approx \frac{\partial q_N}{\partial \alpha_N} \Delta \alpha_N \\
&= 0.20
\end{aligned}
$$

which, looking at Fig. 14 (the exact value is 0.245), is a reasonable answer. [Bear in mind that we have not yet considered the possible change in density induced by the change in β. We come to this shortly.]

Notice that, according to Eq.(75), a negative change in the α of a site *always leads to an accumulation of electron density at that site*. This is a general result of the perturbation theory.

One can similarly work out the change in bond-order p_{rs} between two sites r and s, due to a change in H_{tu} (the same change must occur in H_{ut} to keep things symmetric). For example

a β parameter may be varied between atoms t and u. We find:

$$p_{rs} = \sum_i f_i c_r^{(i)} c_s^{(i)} \tag{80}$$

$$\frac{\partial p_{rs}}{\partial H_{tu}} = \sum_i f_i \left(\frac{\partial c_r^{(i)}}{\partial H_{tu}} c_s^{(i)} + c_r^{(i)} \frac{\partial c_s^{(i)}}{\partial H_{tu}} \right) \tag{81}$$

with

$$\frac{\partial c_r^{(i)}}{\partial H_{tu}} = {\sum_j}' \frac{(\partial U/\partial H_{tu})_{ji}}{\epsilon_i - \epsilon_j} c_r^{(j)} \tag{82}$$

Similar formulae hold for the symmetric charge in H_{ut}, i.e.:

$$\partial p_{rs}/\partial H_{ut} \text{ and } \partial c_r^{(i)}/\partial H_{ut}$$

[Just substitute tu for ut].

In this case, the perturbation occurs between off-diagonal matrix elements:

$$(\partial U/\partial H_{tu})_{ji} + (\partial U/\partial H_{ut})_{ji} = c_u^{(j)} c_t^{(i)} + c_t^{(j)} c_u^{(i)}$$

Substituting, rearranging, and summing we finally obtain:

$$\frac{\partial p_{rs}}{\partial H_{tu}} + \frac{\partial p_{rs}}{\partial H_{ut}} = 2 \sum_{i \in occ} \sum_{j \in unocc} \frac{c_u^{(j)} c_t^{(i)} + c_t^{(j)} c_u^{(i)}}{\epsilon_i - \epsilon_j} (c_r^{(j)} c_s^{(i)} + c_r^{(i)} c_s^{(j)})$$

We can now use this to compute the change in the density on the N atom (i.e. $r = s = 1$) due to the change in β's with C atom 2:

$$\frac{\partial p_{11}}{\partial H_{12}} + \frac{\partial p_{11}}{\partial H_{12}} = 2 \sum_{i=1}^{3} \sum_{j=4}^{6} \frac{c_1^{(j)} c_2^{(i)} + c_2^{(j)} c_1^{(i)}}{\epsilon_i - \epsilon_j} (2 c_1^{(j)} c_1^{(i)})$$

You can verify that the only non-zero terms come from $i = 1, j = 4$ and $i = 2, j = 6$. These give

$$= 4 \left[\underbrace{\frac{\frac{2}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}} - \frac{1}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}}}{3\beta} \cdot \frac{2}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}}}_{(i=1,j=4)} + \underbrace{\frac{\frac{1}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}} - \frac{2}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}}}{3\beta} \cdot \frac{2}{\sqrt{12}} \cdot \frac{1}{\sqrt{6}}}_{(i=2,j=6)} \right]$$

$$= 0$$

The answer turns out to be zero, since the energy gap $\epsilon_1 - \epsilon_4$ coincidentally equals $\epsilon_2 - \epsilon_6 = 3\beta$.

Differential form for the energy

It is possible to cast the expression for the total energy in a useful form in term of the populations and bond-orders. Since:

$$
\begin{aligned}
E &= \sum_{i \in occ} \epsilon_i \\
&= \sum_i f_i \epsilon_i
\end{aligned}
\tag{83}
$$

and for real normalised orbitals:

$$
\begin{aligned}
\epsilon_i &= \langle \psi_i | H | \psi_i \rangle \\
&= \langle \sum_r c_r^{(i)} \phi_r | H | \sum_s c_s^{(i)} \phi_s \rangle \\
&= \sum_r c_r^{(i)} c_r^{(i)} \langle \phi_r | H | \phi_r \rangle + \sum_{r \neq s} c_r^{(i)} c_s^{(i)} \langle \phi_r | H | \phi_s \rangle \\
&= \sum_r |c_r^{(i)}|^2 \alpha_r + \sum_{r \neq s} c_r^{(i)} c_s^{(i)} H_{rs} \\
&= \sum_r |c_r^{(i)}|^2 \alpha_r + 2 \sum_{r > s} c_r^{(i)} c_s^{(i)} H_{rs}
\end{aligned}
\tag{84}
$$

where by writing α_r and H_{rs} we have explicitly allowed for the possible variation of the α's along the molecule, and β's between specific pairs of sites. The sums of r and r, s refer to sums over atomic sites. Noting that:

$$
\begin{aligned}
\sum_i f_i |c_r^{(i)}|^2 &= q_r \\
\sum_i f_i c_r^{(i)} c_s^{(i)} &= p_{rs}
\end{aligned}
$$

Substituting into Eq.(83) and switching the order of summations, we obtain:

$$
\begin{aligned}
E &= \sum_i f_i \left(\sum_r |c_r^{(i)}|^2 \alpha_r + 2 \sum_{r > s} c_r^{(i)} c_s^{(i)} H_{rs} \right) \\
&= \sum_r q_r \alpha_r + 2 \sum_{r > s} p_{rs} H_{rs}
\end{aligned}
\tag{85}
$$

The usefulness of this expression stems from the fact that we can *estimate changes in the total energy induced by changes in the α or β's*. Taking α_r and H_{rs} as independently variable parameters, we can obtain the derivatives of the total energy wrt to them:

$$
\begin{aligned}
\frac{\partial E}{\partial \alpha_r} &= q_r \\
\frac{\partial E}{\partial H_{rs}} &= 2 p_{rs}
\end{aligned}
$$

In other words, the first-order change in the energy for variations in the α and β of $\Delta\alpha_r$ and ΔH_{rs} can be written as:

$$\Delta E^{(1)} = \sum_r q_r \Delta\alpha_r + 2 \sum_{r>s} p_{rs} \Delta H_{rs} \tag{86}$$

Using this expression, we can immediately write down the first-order change in the energy of hetero-substituted molecules, where we vary one or a few of the α's and β's.

For example, in pyridine, we changed one $\alpha \to \alpha_N = \alpha + \frac{1}{2}\beta$, and two of the $\beta \to 0.8\beta$. According to Eq.(86), we have:

$$\Delta E^{(1)} = \frac{1}{2}\beta \times 1 + \frac{2}{3} \times 2 \times 2 \times (-0.2\beta) = -0.033\beta$$

which can be compared with the first-order perturbation value Eq.(68) and exact diagonalisation exact value, Eq.(61).

A second-order correction to the energy can also be sought in which we account for the variation in q_r (and in principle p_{rs}) upon a variation in α_r (and H_{rs}). Thus, in the first instance, we have:

$$\Delta E^{(2)} = \frac{1}{2} \frac{\partial q_N}{\partial \alpha_N} \Delta\alpha_N^2$$

Having computed this quantity in Eq.(79), we obtain for the 2nd order correction:

$$\Delta E^{(2)} = \frac{1}{2} \cdot \frac{0.4}{\beta} \cdot \frac{\beta}{2} \cdot \frac{\beta}{2} = 0.05\beta$$

This leads to an energy $6\alpha + 8.017\beta$, which is closer to the exact value $6\alpha + 8.032\beta$.

IX. REACTIVITY THEORY

An important use of the differential form of the energy, Eq.(86), regards its use in assessing the reactivity of different sites of a conjugated molecule, towards attack by different types of regents (electrophilic, nucleophilic and homolytic).

Let us start with an interpretation of the first term of Eq.(86), assuming a single site, r is being approached by a reagent. If the regent is an electrophile, it will have the effect of withdrawing electrons from site r, and therefore, in effect be reducing (making more negative) the value of α. Assuming that no other perturbation occurs, we have therefore that the change in energy is:

$$\Delta E \approx q_r \Delta\alpha_r \tag{87}$$

For an electrophile, since $\Delta\alpha_r < 0$, this implies that the largest lowering of energy occurs at sites with the largest population. Conversely, for a nucleophile, we can assume that electrons are pushed away from site r, leading effectively to a positive $\Delta\alpha_r$, and therefore, nucleophilic attack will most likely occur at sites with the smallest population, q.

This idea is useful only when the populations differ from site to site. Such examples do exist, even in pure hydrocarbons with no hetero-atoms. For example, in azulene, one finds the following populations:
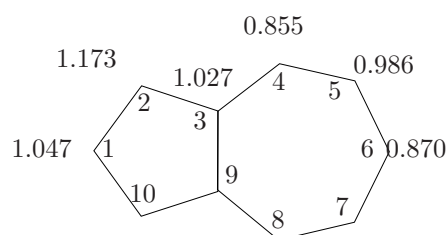

FIG. 15: Populations in azulene according to Hückel theory

According to this picture, we would expect electrophilic attack to occur most likely on sites 2 and 10, and nucleophilic on sites 4 and 8. These predictions are in agreement both with experiment, and also more sophisticated calculations.

On the other hand, the above argument precludes a large class of molecules for which the unperturbed π populations are uniform, namely alternant hydrocarbons. In this case, Eq.(65) is no longer discriminatory with respect to different sites of a molecule. A classic problem, for example, is the most likely position of attack on the naphthalene molecule: Is position 1 more likely to be attacked than position 2?

In such cases, we must resort to the second-order expression:

$$\Delta E \approx q_r \Delta\alpha_r + \frac{1}{2}\pi_r \Delta\alpha_r^2 \tag{88}$$

where π_r is the self-polarisability introduced earlier on:

$$\pi_r = \frac{\partial q_r}{\partial \alpha_r} \tag{89}$$

According to this relation, the site which has a large π_r will be most favoured for attack (by either electrophile or nucleophile, since $\Delta\alpha_r^2$ is positive in both cases). (Remember that $\pi_r < 0$ always, and such 2nd-order corrections always reduce the energy).
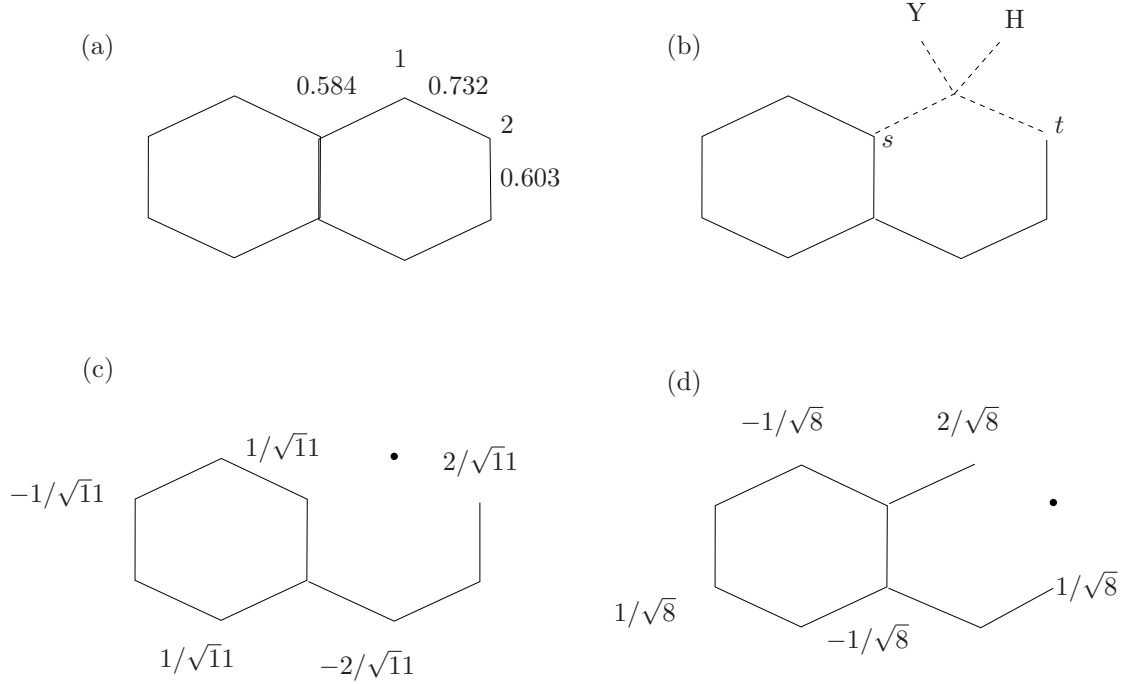
37

FIG. 16: (a) Naphthalene, bonds-orders from 1st order perturbation theory, (b) Transition complex; (c) Residual molecule with site 1 removed and (d) Site 2 removed, showing the coefficients of the non-bonding MO

We had earlier derived a general formula for computing π_r, Eq.(76). The main difficulty is that this equation is awkward to use, since the MOs which appear in this equation refer to the unperturbed - but nevertheless perhaps very complicated - molecule, eg. the unperturbed naphthalene molecule. In practice, we might have to resort to a 'perturbation theory of a perturbation theory', with a consequent reduction in accuracy.

There is a simplification which occurs if the β's are all identical (like naphthalene). In this case, to an excellent approximation, one can show:

$$\pi_r = \frac{2q_r - q_r^2}{2N_r\beta} \tag{90}$$

where N_r is the sum over the bond-orders of the sites attached to r:

$$N_r = \sum_{s\to r} p_{rs} \tag{91}$$

N_r is sometimes known as Dewar's reactivity number, or 'bond number'. (We prefer the latter term). According to this relation, π_r increases as N_r decreases, i.e. sites involved with the least bonding are the most polarisable and hence prone to attack. This equation can sometimes be used if the bond-orders of the molecule are known. For example, for

naphthalene, perturbation theory gives the bond-orders indicated on Fig. 16, from which we can conclude that site 1 would be marginally preferred to site 2 in a substitution reaction.

In fact, the N_r, the bond-number index, is also very useful is assessing the likely position of homolytic attack, e.g. by a neutral radical. In this case the reagent is uncharged, which means that the electric fields are likely to be small, and hence the approach of the attacking molecule will not substantially affect the α's. On the other hand, as it approaches and begins to interact with the molecule, it is likely to weaken the bonds in the neighbourhood of the site being attacked, and therefore increase (i.e. make more positive) the neighbouring β's. In this case, the second set of term in Eq.(86) come into play:

$$\Delta E \approx 2 \sum_{s \to r} p_{rs} \Delta \beta = 2 N_r \Delta \beta \tag{92}$$

In other words, the sites with smallest N_r are, once again, most favourable to this type of attack.

Localisation theory

There is a related approach to assessing reactivity, which is based on the idea of a "transition complex", i.e. a point near the peak of the potential energy curve describing the interaction between the molecule and reagent. For an attack on different positions, the peak heights will in general differ, and the one with the lowest peak will generally be the favoured pathway. How can we estimate the energy of the transition complex, relative to the unperturbed molecule (and reagent)?

Let us assume that the site under attack, r, is taken out of the conjugated π system by the tetrahedrally-coordinated transition complex develops. The local sp^2 geometry at site r will be destroyed, and therefore the π-system itself will be affected, since the previously delocalised MO's will no longer be able to include a finite amplitude on this site. In other words, the "volume" available to π-bonding will be reduced, and there will be a consequent affect on the energy. The change in energy due to this reduction will, however, depend on the position of attack. Therefore, we define a "localisation energy", L_r, to be the difference in π-energy of the residual molecule, E_r consisting of n π-electrons, and original molecule E:

$$L_r = E_r - E \tag{93}$$

To compute the localisation energy, therefore, requires us to compute the energy of the
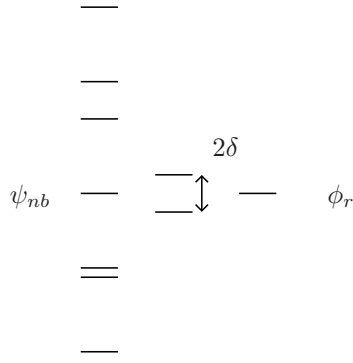
FIG. 17: Energy level diagram of a residual odd-alternant, showing interaction with the non-bonding MO or site r.

residual molecule in which site r has been removed from consideration. This is, in general, quite a tedious task, but for even alternant hydrocarbons a simple (though approximate) route exists to compute directly the difference in energy required by Eq.(93).

The key point is that the residual molecule must be a odd-alternant, and therefore must possess a non-bonding MO, which we shall denote ψ_{nb}, and whose energy is α. To a good approximation, the interaction between the fragment molecule and the site r (which also has energy α) can be considered to be a two level problem, in which the matrix element between them is given by:

$$
\begin{aligned}
H_{12} &= \langle \psi_{nb} | H | \phi_r \rangle \\
&= (c_s^{(nb)} + c_t^{(nb)})\beta
\end{aligned}
$$

where sites t and s are neighbouring to r, and $c_s^{(nb)}$ and $c_t^{(nb)}$ are the coefficients of the non-bonding MO at these two sites. Since we know the The secular determinant for such a two-level system gives the energy, δ which arises out of the mixing of these two states:

$$
\begin{vmatrix} -\delta & H_{12} \\ H_{12} & -\delta \end{vmatrix} = 0
$$

which, solving, gives:

$$
\delta = \pm H_{12} = \pm(c_s^{(nb)} + c_t^{(nb)})\beta
$$

Therefore, according to this relation, the energy of the residual fragment ought to be higher than the whole molecule by an amount given by twice this (two electrons are destabilised), i.e.

$$
L_r = -2(c_s^{(nb)} + c_t^{(nb)})\beta
$$

40

This approximation is remarkably easy to use, since we already know that the coefficients of the non-bonding MO in the residual molecule are very easy to compute [See Section VI]. For the two sites of naphthalene under consideration, they are given in Fig 16. In this case, we can see that the localisation energies are:

$$
\begin{aligned}
L_1 &= -2\beta \frac{3}{\sqrt{11}} \\
L_2 &= -2\beta \frac{3}{\sqrt{8}}
\end{aligned}
$$

therefore we conclude that site 1 has a more favourable localisation energy, and is more likely to be substituted. This is in agreement with our earlier calculation based on π_r, and also in agreement with experiment.

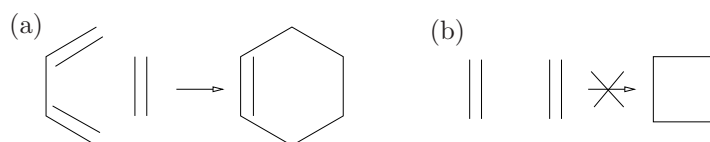## X. ORBITAL CORRELATION DIAGRAMS: APPLICATIONS TO PERICYCLIC REACTIONS

FIG. 18: (a) Diels-Alder cycloaddition readily occurs; (b) Concerted dimerisation of ethene is difficult

Several types of reactions, including cyclo-additions, ring openings/closures, can be rationalised in terms of correlation diagrams of the underlying MOs as the reaction proceeds. For example, it is known that 4+2 (Diels-Alder) cyclo-additions occur readily, whereas the corresponding 2+2 reaction is forbidden. Why should this be? Presumably, the latter reaction encounters a substantial barrier which is not present in the former - can the presence or absence of large barriers be understood solely in terms of the underlying MO's?

The answer turns out to be "yes", and appears to be related to the presence of symmetry in the reacting systems. Let us first consider the 2+2 system. Let us draw the MO's of the unreacted and reacted systems. The former has two sets of ethelyic π orbitals, whereas the latter has newly-formed σ orbitals (Fig. 19).

In the unreacted state, the ground-state configuration is $(a_g)^2(b_{3u})^2$. Maintaining the same occupancy would lead to the double occupation of an excited state in ring structure. But even if the double occupation of the b_{3u} is not maintained all the way, but only until
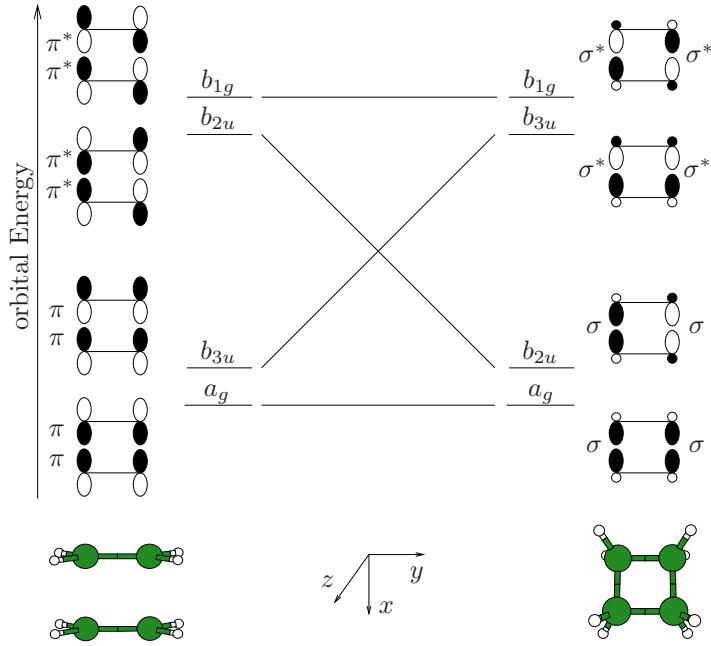
FIG. 19: D_{2h} symmetry is conserved if the 4 C atoms remain in-plane. The MO's in the unreacted (left) and reacted (right) are labelled according to their symmetry (irrep) in this point group.

the transition state, (somewhere midway on this diagram), the energy of the system is is substantially higher than initial state. As a result, the reaction is forbidden if the starting molecule is in the ground-state. On the other hand, if the molecule is photo-excited initially, promoting an electron from $b_{3u} \rightarrow b_{2u}$, the reaction proceeds without an unduly large barrier. This reaction is photo-active.

The overall picture can be summarised in terms of a *state correlation diagram*, in which the total electronic wavefunction of the system is followed. In the present case, we can construct three such complete wavefunctions, corresponding to:

$$\text{Ground state } \Psi_0 \quad (A_g): \ a_g^2 b_{3u}^2$$
$$\text{Singly excited } \Psi_1 \quad (B_{1g}): \ a_g^2 b_{3u}^1 b_{2u}^1$$
$$\text{Doubly excited } \Psi_2 \quad (A_g): \ a_g^2 b_{2u}^2$$

There are other higher-energy states we could construct, but they are not relevant.

Since the ground-state and the doubly excited state are of the same symmetry, they can
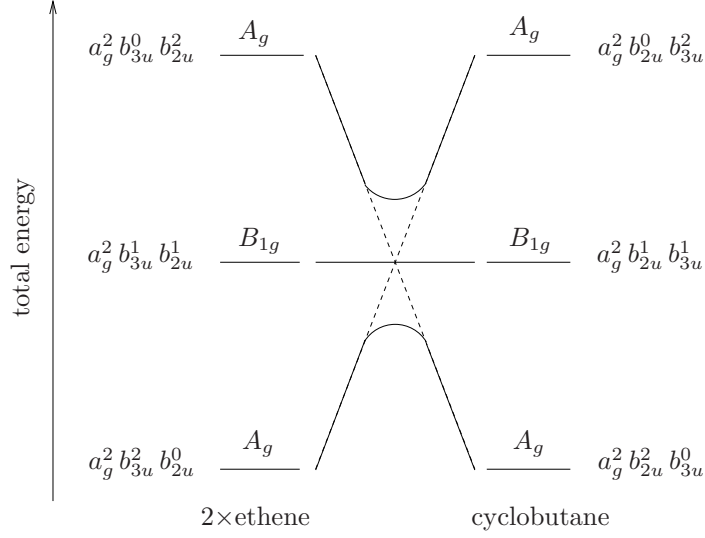
$$a_g^2\, b_{3u}^0\, b_{2u}^2 \quad \underline{}^{A_g} \qquad\qquad ^{A_g}\underline{} \quad a_g^2\, b_{2u}^0\, b_{3u}^2$$

$$a_g^2\, b_{3u}^1\, b_{2u}^1 \quad \underline{\phantom{B_{1g}}}^{B_{1g}} \qquad\qquad \phantom{B_{1g}}^{B_{1g}}\underline{\phantom{B_{1g}}} \quad a_g^2\, b_{2u}^1\, b_{3u}^1$$

$$a_g^2\, b_{3u}^2\, b_{2u}^0 \quad \underline{}^{A_g} \qquad\qquad ^{A_g}\underline{} \quad a_g^2\, b_{2u}^2\, b_{3u}^0$$

$2\times$ethene $\qquad\qquad$ cyclobutane

FIG. 20: State correlation diagram

mix, and do so quite substantially as they become energetically close. If we let

$$
\begin{aligned}
E_0 &= H_{00}^{(N)} = \text{Energy of } \Psi_0 \\
E_2 &= H_{22}^{(N)} = \text{Energy of } \Psi_2 > E_0 \\
U &= H_{02}^{(N)} = \text{interaction matrix element}(\neq 0 \text{ by hypothesis})
\end{aligned}
$$

then the secular equations become:

$$
\begin{vmatrix}
E_0 - E & U \\
U & E_2 - E
\end{vmatrix} = 0
$$

whose solutions for E are:

$$
\begin{aligned}
E &= \frac{E_0 + E_2}{2} \pm \frac{1}{2}\sqrt{(E_0 - E_2)^2 + 4U^2} \\
&= \frac{E_0 + E_2}{2} \pm \frac{(E_0 - E_2)}{2}\sqrt{1 + \left(\frac{2U}{E_0 - E_2}\right)^2}
\end{aligned}
\tag{94}
$$

If $|U| << |E_0 - E_2|$ then we can Taylor expand the $\sqrt{}$ to get:

$$
E \approx \frac{E_0 + E_2}{2} \pm \frac{(E_0 - E_2)}{2}\left(1 + \frac{1}{2}\frac{4U^2}{(E_0 - E_2)^2}\right)
\tag{95}
$$

which for the ground-state becomes:

$$
E \approx E_0 + \frac{U^2}{E_0 - E_2}
\tag{96}
$$

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(note $E_0 - E_2 < 0$), whilst the doubly-excited state goes as

$$E \approx E_2 - \frac{U^2}{E_0 - E_2} \tag{97}$$

In other words, the two states repel each other, irrespective of the sign of U; the ground-state is lowered in energy and the excited state pushed up. This is the basis for the non-crossing rule for states with the same symmetry. The first excited state, being of a different symmetry, is unaffected. The magnitude of the repulsion depends both on $|U|$ and on the energy difference denominator, the latter growing as the transition state increases. The effect of the configuration interaction is most noticeable at transition states.

Nevertheless, even with the above lowering of energy, there remains a large barrier (compared to the thermal energy availble to the molecules) to reaction for the ground-state, and ethene dimerisation remains thermally forbidden.

The same considerations hold for example in reactions such as $H_2 + I_2$, long thought to proceed in a concerted fashion via a rectangular transition state, but in fact shown experimentally to involve iodine atoms. The concerted reaction has a high barrier, which can be rationalised analogously to the ethene dimerisation problem.

Turning now to the [4+2] cycloaddition, we construct an the orbital correlation diagram, labelling the MO's according to their behaviour under σ_v (Fig. 21).
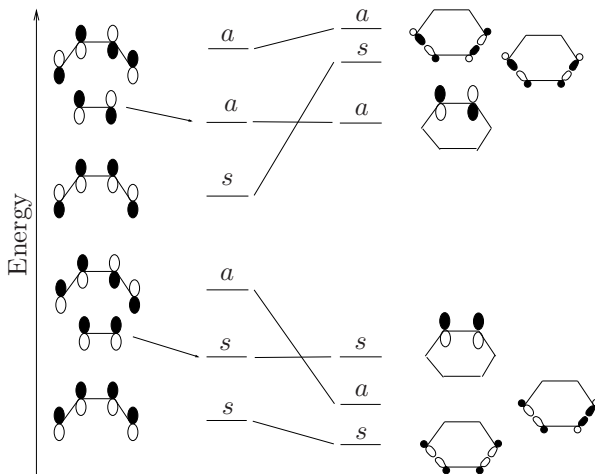

FIG. 21: On the LHS, the p_π-based MO's of the reacting species are labelled symmetric (s) or antisymmetric (a) under the action of a vertical mirror plane, assuming a symmetrical transition state. On the RHS, the product, whose MOs now also have σ character in the newly formed bonds, are similarly labelled.

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It can be seen that the occupied levels in the reactant and product correlate with each other, as opposed to the case of the [2+2] dimerisation. In this case, the reaction can proceed with little barrier, and is therefore thermally accessible.

Similar considerations work for ring opening and closing, see problem 16, where "conrotatory" and "disrotatory" mechanisms can be allowed or forbidden, which leads to methods for selective synthesis of cis or trans products.

XI. AN IMPORTANT FAILURE OF MO THEORY: MOLECULAR DISSOCIATION

Thus far we have dealt with some (great) successes of MO theory, even specialised to its Hückel form. The impression should not be given, however, that the theory is always correct, even qualitatively. The principal and ultimate shortcoming of the method comes from the lack of proper treatment of electron-electron interactions, the latter manifesting itself in important *electron correlation* phenomena which no one-electron theory - however sophisticated - can describe. The aim of this section is to give an account of one of the most important examples of such failures. Although one could choose examples from hydrocarbon chemistry, the standard example actually occurs in the simplest of chemical systems, namely the H_2 molecule.

Consider the H_2 molecule, whose complete MO wavefunction is written is in terms of the MO's of the molecule:

$$
\begin{aligned}
\psi_1 &= \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \\
\psi_2 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)
\end{aligned}
\tag{98}
$$

where ϕ_1 and ϕ_2 refer to the (normalised) 1s orbital on atom 1 and 2 respectively. [Note the analogy with the ethelene system here. Instead of using p_z orbitals, we are using s orbitals. This, of course, affects the numerical values of the α and β integrals, but does not much affect the structure of the theory].

These two states are, of course, the $1\sigma_g$ and $1\sigma_u^*$ bonding and anti-bonding orbitals you are very familiar with, but we prefer to use the ψ_i notation to keep things general.

Let us try to construct the *total* ground-state (electronic) wavefunction for the H_2 molecule. We denote the total wavefunction as Ψ, and note that it will be dependent on the coordinates

and spins of two electrons:

$$\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2) \tag{99}$$

In what follows, we will refer to $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ simply as $\Psi(1, 2)$.

Since both electrons occupy the bonding orbital ψ_1, but with opposite spins, we can try to construct the wavefunction by placing electron 1 in an α spin-state and electron 2 in a β spin state:

$$\Psi(1, 2) = \psi_1(1)\alpha(1) \times \psi_1(2)\beta(2) \tag{100}$$

You should immediately object to this wavefunction: it does not obey the Pauli principle, that if we interchange the labels of electron 1 and 2, then the wavefunction should simply change sign, which it manifestly does not:

$$\Psi(2, 1) = \psi_1(2)\alpha(2) \times \psi_1(1)\beta(1) \neq -\Psi(1, 2) \tag{101}$$

What we have done if to assign electron 2 to spin α, and electron 1 to the spin β. We use subscripts to denote the spatial orbitals, whilst the labels of individual electrons is placed in round brackets, eg (1) or (2).

There is a simple recipe to construct anti-symmetric wavefunction, which is to use a determinant. Let us first begin by constructing the two possible *spin-orbitals*:

$$\begin{aligned} \chi_1 &= \psi_1\alpha \\ \chi_2 &= \psi_1\beta \end{aligned} \tag{102}$$

If electron 1 is inserted in χ_1 we get

$$\chi_1(1) = \psi_1(1)\alpha(1) \tag{103}$$

and if it is inserted in χ_2, we would get:

$$\chi_2(1) = \psi_1(1)\beta(1) \tag{104}$$

Similarly, if we insert electron 2 into χ_1 and χ_2 respectively, we obtain

$$\chi_1(2) = \psi_1(2)\alpha(2), \qquad \chi_2(2) = \psi_1(2)\beta(2). \tag{105}$$

Note that the χ_i are ortho-normal, e.g.:

$$\begin{aligned} \langle \chi_1 | \chi_1 \rangle &= \langle \psi_1 | \psi_1 \rangle \langle \alpha | \alpha \rangle = 1 \\ \langle \chi_1 | \chi_2 \rangle &= \langle \psi_1 | \psi_1 \rangle \langle \alpha | \beta \rangle = 0 \end{aligned}$$

When you have two-electron bra-kets, you need to take care of the electron labels as well, by gathering each electron label into its own bra-ket. E.g.

$$\langle \chi_2(1)\chi_1(2)|\chi_1(1)\chi_2(2)\rangle \; = \; \langle \chi_2(1)|\chi_1(1)\rangle \times \langle \chi_1(2)|\chi_2(2)\rangle$$

which in this case equals 0.

Let us construct the following determinant:

$$\Psi(1,2) = \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix}$$

Why does this help? Consider exchanging the labels of the two electrons:

$$\Psi(2,1) = \begin{vmatrix} \chi_1(2) & \chi_2(2) \\ \chi_1(1) & \chi_2(1) \end{vmatrix}$$

You can see that this amounts to exchanging two rows of a determinant. Recall that this operation *changes the sign of the the determinant*:

$$\Psi(2,1) = \begin{vmatrix} \chi_1(2) & \chi_2(2) \\ \chi_1(1) & \chi_2(1) \end{vmatrix} = - \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = -\Psi(1,2)$$

Note, also, that if we place both electrons into the *same* spin-orbital, the determinant vanishes identically (two columns would be identical). This form of wavefunction, therefore, also forbids multiple occupation of spin-orbitals (as it should).

This means that we now have, at least, a wavefunction $\Psi(1,2)$ which is acceptable to Pauli. Let us expand the determinant:

$$\Psi(1,2) = \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)$$

Is it normalised? No:

$$\begin{aligned}
\langle \Psi(1,2)|\Psi(1,2)\rangle \; &= \; \langle \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)|\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)\rangle \\
&= \; \langle \chi_1(1)\chi_2(2)|\chi_1(1)\chi_2(2)\rangle - \langle \chi_1(1)\chi_2(2)|\chi_1(2)\chi_2(1)\rangle \\
&\quad - \langle \chi_1(2)\chi_2(1)|\chi_1(1)\chi_2(2)\rangle + \langle \chi_1(2)\chi_2(1)|\chi_1(2)\chi_2(1)\rangle
\end{aligned}$$

Note that:

$$\begin{aligned}
\langle \chi_1(1)\chi_2(2)|\chi_1(2)\chi_2(1)\rangle \; &= \; \langle \chi_1(1)|\chi_2(1)\rangle \times \langle \chi_2(2)|\chi_1(2)\rangle \\
&= \; 0
\end{aligned}$$

whilst

$$\langle \chi_1(1)\chi_2(2)|\chi_1(1)\chi_2(2)\rangle = 1$$

Therefore we get:

$$\langle \Psi(1,2)|\Psi(1,2)\rangle = 2$$

i.e. to get a normalised $\Psi(1,2)$ we need to divide by $\sqrt{2}$:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} \tag{106}$$

In terms of ψ_1 and the spin functions, we have:

$$
\begin{aligned}
\Psi(1,2) &= \frac{1}{\sqrt{2}} \left[\underbrace{\psi_1(1)\alpha(1)}_{\chi_1(1)} \underbrace{\psi_1(2)\beta(2)}_{\chi_2(2)} - \underbrace{\psi_1(2)\alpha(2)}_{\chi_1(2)} \underbrace{\psi_1(1)\beta(1)}_{\chi_2(1)} \right] \\
&= \frac{\psi_1(1)\psi_1(2)}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \tag{107}
\end{aligned}
$$

You will immediately recognise this as a singlet ($S = 0$) state. Given that ψ_1 has σ symmetry, this implies that the corresponding term symbol is $^1\Sigma_g^+$.

Now, what is the difficulty with this wavefunction? Let us expand it now in terms of the AO's ϕ_1 and ϕ_2. Since $\psi_1 = (\phi_1 + \phi_2)/\sqrt{2}$, we have:

$$\Psi(1,2) = \frac{1}{(\sqrt{2})^3} \left[\phi_1(1) + \phi_2(1) \right] \left[\phi_1(2) + \phi_2(2) \right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right]$$

Expanding the product over the spatial orbitals, we get (omitting the spin wavefunction to reduce clutter):

$$\Psi(1,2) \sim \left[\underbrace{\phi_1(1)\phi_1(2)}_{ionic} + \underbrace{\phi_1(1)\phi_2(2)}_{biradical} + \underbrace{\phi_2(1)\phi_1(2)}_{biradical} + \underbrace{\phi_2(1)\phi_2(2)}_{ionic} \right] \tag{108}$$

What is the interpretation of the terms above? The first term puts electron 1 and electron 2 both in AO ϕ_1, i.e. the 1s orbital belonging to one of the nuclei. The 4th term, similarly, puts both electrons about the second nucleus. The middle two terms place one electron on one nucleus, and the second electron on the other. One can think of these as the following chemical entities:

$$\text{H}^- \quad \text{H}^+, \qquad \text{H}\cdot \quad \text{H}\cdot, \qquad \text{H}^+ \quad \text{H}^-$$

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In other words, this wavefunction cannot describe *molecular dissociation* properly, since it retains these ionic (i.e. H^- H^+) components even in that limit. These components have a high electron-electron repulsion energy. The energy of such a wavefunction is much too high compared to its exact value (which in thse case of dissociated H_2 is 1 Hartree). In the exact wavefunction, the probablity of finding two electrons around the same nucleus is very small, compared to that (50%) implied by the MO wavefunction. In other words, in order to improve the description of molecular dissociation, one must introduce *electron correlation*, such that if one electron finds itself around one nucleus, the other electron has an enhanced probability of finding itself around the other nucleus.

How can one introduce such electron correlation? Let us note that the single-determinant description of the two-electron wavefunction is itself an approximation. We may be able to do better by mixing other determinants into the present one, to yield a better overall wavefunction. Let us denote the above, approximate, wavefunction as Ψ_0. Then we would expect the "exact" wavefunction to be written as

$$\Psi_{exact}(1,2) = \Psi_0(1,2) + \sum_I c_I \Psi_I(1,2) \tag{109}$$

where $\Psi_I(1,2)$ are determinants constructed out of the *unoccupied* manifold of MOs, and c_I are coefficients to be determined by the variational principle. This method of introducing electron correlation is called *configuration interaction*.

In the present case, we can construct a determinant by doubly-occupying the anti-bonding orbital $\psi_2 = (\phi_1 - \phi_2)/\sqrt{2}$:

$$\Psi_2(1,2) = \frac{1}{\sqrt{2}} \psi_2(1)\psi_2(2).\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Substituting for ψ_2 we get:

$$
\begin{aligned}
\Psi_2(1,2) &\sim \left[\phi_1(1) - \phi_2(1)\right]\left[\phi_1(2) - \phi_2(2)\right] \\
&= \left[\phi_1(1)\phi_1(2) - \phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2) + \phi_2(1)\phi_2(2)\right]
\end{aligned}
$$

Notice that in Ψ_2, the "ionic" components of the wavefunction come with the opposite sign to the "bi-radical" parts of the wavefunction.

Therefore, if we subtract Ψ_2 from Ψ_0, we remove the troublesome ionic factors, leaving (apart from normalisation factors):

$$\Psi_0 - \Psi_2 = \left[\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \tag{110}$$

which dissociates correctly. Eq.(110) is the simplest example of a configuration-interaction wavefunction. The energy of this wavefunction is significantly lower than that of Ψ_0 at dissociation. One can equally ask about the contribution of Ψ_2 in the undissociated molecule. In this case, one needs to solve the secular equation (which arise from the variational principle, exactly as we did for the Hückel system) owing to mixing of these two states. Let us define

$$H_{ij}^{(N)} = \langle \Psi_i | H^{(N)} | \Psi_j \rangle$$

where the $H^{(N)}$ is complete (electronic) Hamiltonian for the system (i.e. the N-electron Hamiltonian, not the one-electron Hamiltonian we normally deal with). This Hamiltonian contains explicitly the electron-electron repulsion terms which are either absent (or dealt with in an approximate way) in the one-electron hamiltonian.

The analysis proceeds almost identically as the state-correlation analysis we performed for the ethene dimerisation. If we let

$$
\begin{aligned}
E_0 &= H_{00}^{(N)} = \text{Energy of } \Psi_0 \\
E_2 &= H_{22}^{(N)} = \text{Energy of } \Psi_2 > E_0 \\
U &= H_{02}^{(N)} = \text{interaction matrix element}
\end{aligned}
$$

then the secular equations become:

$$
\begin{vmatrix}
E_0 - E^{(CI)} & U \\
U & E_2 - E^{(CI)}
\end{vmatrix} = 0
$$

whose solutions lead to:

$$E^{(CI)} = \frac{E_0 + E_2}{2} \pm \frac{1}{2}\sqrt{(E_0 - E_2)^2 + 4U^2}$$

i.e. (cf Eqs.(94,95)):

$$E_0^{(CI)} \approx E_0 + \frac{U^2}{E_0 - E_2}$$

and

$$E_2^{(CI)} \approx E_2 - \frac{U^2}{E_0 - E_2}$$

Notice that this result is what we would expect from non-degenerate perturbation theory! Similarly, you can also show that the component of Ψ_2 in Ψ^{CI} is $\approx U/(E_0 - E_2)$ for small $|U/(E_0 - E_2)| << 1$, i.e. in this limit:

$$\Psi_0^{CI} \approx \Psi_0 + \frac{U}{E_0 - E_2}\Psi_2$$

One can further refine the Full-CI wavefunction by enlarging the basis and constructing other (indeed all) possible excited-state determinants which have the same symmetry and spin ($^1\Sigma_g^+$) as Ψ_0. This provides, in principle, a systematic technique to introduce correlation. However, it is not in general a practical method, because the number of possible excited-state determinants grows in an factorial (i.e. exponential) manner (both with number of basis functions and the number of electrons). Methods to treat accurately electron correlation remains one of the most active and challenging areas of Theoretical Chemistry.

XII.   MOLECULAR VIBRATIONS

The final topic – molecular vibrations – we will cover appears very different to Hückel theory, but in fact has very close parallels it which enable us to transfer our knowledge from area to another.

Given a molecule in a stable geometry, the nuclei which constitute the molecule exhibit small-amplitude vibrations about the equilibrium geometry. You will, of course, have met the group-theoretical analysis of molecular vibrations in part IB. For example, if we take the C-H stretching modes of the benzene molecule, and set up a basis of displacements $\Delta_1, \Delta_2, ..., \Delta_6$, these can be reduced by analysis of the characters
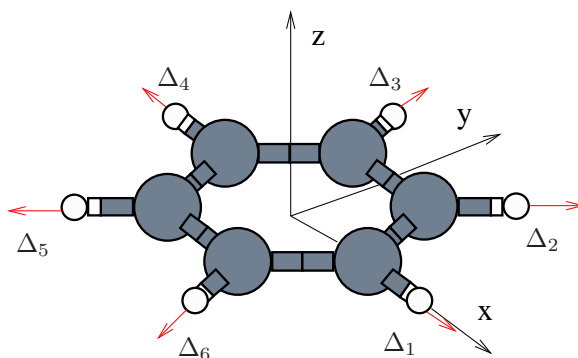

FIG. 22: Basis for C-H stretching modes

$$
\begin{array}{c|ccccccccccccc}
D_{6h} & E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \\
\hline
\Gamma_{p_z} & 6 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 6 & 0 & 2
\end{array}
\tag{111}
$$

to

$$\Gamma_\Delta = A_{1g} + E_{2g} + B_{1u} + E_{1u}$$

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you can verify that symmetry-adapted linear combinations of the displacements can be set up as follows:

$$Q_{A_{1g}} = \frac{1}{\sqrt{6}} (\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4 + \Delta_5 + \Delta_6)$$

$$Q_{E_{2g}}^{(1)} = \frac{1}{2} (\Delta_2 - \Delta_3 + \Delta_5 - \Delta_6)$$

$$Q_{E_{2g}}^{(2)} = \frac{1}{\sqrt{12}} (2\Delta_1 - \Delta_2 - \Delta_3 + 2\Delta_4 - \Delta_5 - \Delta_6)$$

$$Q_{E_{1u}}^{(1)} = \frac{1}{\sqrt{12}} (2\Delta_1 + \Delta_2 - \Delta_3 - 2\Delta_4 - \Delta_5 + \Delta_6)$$

$$Q_{E_{1u}}^{(2)} = \frac{1}{2} (\Delta_2 + \Delta_3 - \Delta_5 - \Delta_6)$$

$$Q_{B_{1u}} = \frac{1}{\sqrt{6}} (\Delta_1 - \Delta_2 + \Delta_3 - \Delta_4 + \Delta_5 - \Delta_6)$$

These symmetry-adapted displacements can be regarded as approximations to the "normal modes" of the molecule, which are analogous to the MOs which we obtain by solving Hückel secular determinants. The question is, for the vibrational problem, what is the analogous secular determinant, and from where does it arise?

A.   Revision of the simple harmonic oscillator

To begin with, let us remind ourselves of the important properties of a one-dimensional harmonic oscillator. We suppose we have a particle of mass m moving in a potential given by $V(x) = \frac{1}{2}kx^2$. The Hamiltonian is:

$$H = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$$

Classically, the particle obeys Newton's Law, which states that:

$$m\ddot{x} = -\frac{dV}{dx}$$

giving rise to the familiar equation of motion:

$$m\ddot{x} = -kx$$

Solutions to this equation have the form [verify]:

$$x(t) = A\cos(\omega t + \phi)$$

where

$$\omega = \sqrt{\frac{k}{m}} \tag{112}$$

In other words, the particle executes oscillatory motion with angular frequency given by Eq.(112). A and ϕ are constants determined by the initial conditions of the problem (eg initial position and velocity).

Note that we can cast the Hamiltonian in the form:

$$H = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2$$

The quantum harmonic oscillator has quantized energy levels at

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right)$$

with ω given by the classical result, Eq.(112). It has a zero-point energy of $\hbar\omega/2$.

B. A diatomic molecule

So far so good. Let us now take a slightly more complicated problem. Consider a *diatomic molecule* with (possibly unequal) masses m_1, m_2, interacting with a potential that can be described harmonically with a force constant k. Assuming that the motion of the two nuclei is confined to one dimension, the Hamiltonian of the problem becomes:

$$H = \frac{1}{2}\sum_i m_i \dot{x}_i^2 + \underbrace{\frac{1}{2}k(x_1 - x_2)^2}_{V(x_1,x_2)} \tag{113}$$

where x_1 and x_2 are the displacement coordinates relative to the equilibrium geometry of the molecule. What is the motion of the two particles? Of course we know how to proceed, by transforming into the centre-of-mass and relative coordinates, and solving the problem therein. This leads to simple harmonic motion in the relative coordinates, with frequency $\sqrt{k/\mu}$, where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the diatomic, a result you should be familar with.

FIG. 23: Displacement coordinates for a diatomic

However, here we will pursue a different path which enables generalisation to more complex problems. Our aim is perform *coordinate-transformations* of the type

$$x_i = c_i^{(1)}Q_1 + c_i^{(2)}Q_2, \qquad \text{for } i = 1, 2$$

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so as to convert the Hamiltonian Eq.(113) into the form:

$$H = \sum_i \left(\frac{1}{2}\dot{Q}_i^2 + \frac{1}{2}\omega_i^2 Q_i^2 \right) \tag{114}$$

i.e. (in this case two) *uncoupled* harmonic oscillators in the transformed variables Q_1, Q_2, and whose motions are given by:

$$Q_i(t) = A_i \cos(\omega_i t + \phi_i)$$

where ω_i is the corresponding angular frequency for "mode" i. .

The remarkable aspect is that these coordinate transformations turn to be nearly perfectly analogous to the problem of finding MOs from AOs in Hückel theory!

First, we transform to *mass-weighted coordinates*:

$$q_i = \sqrt{m_i} x_i \tag{115}$$

which results in the mass factors being removed from the KE term:

$$H = \frac{1}{2}\sum_i \dot{q}_i^2 + \frac{1}{2}k \left(\frac{q_1}{\sqrt{m_1}} - \frac{q_2}{\sqrt{m_2}} \right)^2 \tag{116}$$

This can now be cast in the form [verify!]:

$$H = \frac{1}{2}\sum_i \dot{q}_i^2 + \frac{1}{2}\sum_{ij} q_i K_{ij} q_j \tag{117}$$

where K is the following matrix:

$$K = \begin{bmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} \\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} \end{bmatrix} \tag{118}$$

called the *dynamical or Hessian matrix*.

Since we are looking for uncoupled Hamiltonians of the form Eq.(114), let us suppose that we have solved for the eigenvectors (and eigenvalues) of the Hessian, i.e. we have in hand the following:

$$\sum_j K_{ij} c_j^{(n)} = \lambda_n c_i^{(n)} \tag{119}$$

where $c_i^{(n)}$ is the i-th component of the n-th (normalised) eigenvector, and λ_n the corresponding eigenvalue. Recall that such eigenvectors are orthonormal:

$$\sum_i c_i^{(n)} c_i^{(m)} = \delta_{nm} \tag{120}$$

What use are these eigenvectors? If we let

$$q_i = \sum_n c_i^{(n)} Q_n \qquad (121)$$

and substitute into the second term of Eq.(117) we obtain:

$$\sum_{ij} q_i K_{ij} q_j = \sum_{ij} \left[\sum_n c_i^{(n)} Q_n \right] K_{ij} \left[\sum_m c_j^{(m)} Q_m \right] \qquad (122)$$

Rearranging the sums:

$$
\begin{aligned}
\sum_{ij} \left[\sum_n c_i^{(n)} Q_n \right] K_{ij} \left[\sum_m c_j^{(m)} Q_m \right] &= \sum_{nm} Q_n \left[\sum_{ij} c_i^{(n)} K_{ij} c_j^{(m)} \right] Q_m \\
&= \sum_{nm} Q_n \lambda_m \delta_{nm} Q_m \\
&= \sum_n \lambda_n Q_n^2 \qquad (123)
\end{aligned}
$$

In other words, the transformation Eq.(121) casts the terms in precisely the required diagonal form of Eq.(114), as long as we make the identification:

$$\lambda_n = \omega_n^2 \qquad (124)$$

The KE terms are unaffected by the transformation, and remain in diagonal form:

$$
\begin{aligned}
\sum_i \dot{q}_i^2 &= \sum_i \left[\sum_n c_i^{(n)} \dot{Q}_n \right] \left[\sum_m c_i^{(m)} \dot{Q}_m \right] \\
&= \sum_{nm} \dot{Q}_n \left[\sum_i c_i^{(n)} c_i^{(m)} \right] \dot{Q}_m \\
&= \sum_{nm} \dot{Q}_n \delta_{nm} \dot{Q}_m \\
&= \sum_n \dot{Q}_n^2
\end{aligned}
$$

In other words, finding the eigenvectors/values of the Hessian matrix completely solves the problem. Let us therefore proceed with this task for the diatomic system. The secular equation are:

$$
\begin{vmatrix}
\frac{k}{m_1} - \lambda & -\frac{k}{\sqrt{m_1 m_2}} \\
-\frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} - \lambda
\end{vmatrix} = 0 \qquad (125)
$$

leading to:

$$\left(\frac{k}{m_1} - \lambda \right) \left(\frac{k}{m_2} - \lambda \right) - \frac{k^2}{m_1 m_2} = 0$$

i.e.

$$\lambda^2 - \lambda \left(\frac{k}{m_1} + \frac{k}{m_2} \right) + \frac{k^2}{m_1 m_2} - \frac{k^2}{m_1 m_2} = 0$$

which is solved by:

$$\lambda_1 = 0,$$
$$\lambda_2 = \left(\frac{k}{m_1} + \frac{k}{m_2} \right)$$

or, if we write:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and recall that $\lambda_n = \omega_n^2$ (Eq.(124)), we have

$$\omega_1^2 = 0$$
$$\omega_2^2 = \frac{k}{\mu}$$

in agreement with our expectations. What do these two frequencies physically relate to? The eigenvectors $\mathbf{c}^{(i)}$ satisfy:

For $\omega_1^2 = 0$:

$$\begin{bmatrix} \frac{1}{m_1} & -\frac{1}{\sqrt{m_1 m_2}} \\ -\frac{1}{\sqrt{m_1 m_2}} & \frac{1}{m_2} \end{bmatrix} \mathbf{c}^{(1)} = 0 \quad \rightarrow \quad \mathbf{c}^{(1)} = \frac{1}{\sqrt{M}} \begin{bmatrix} \sqrt{m_1} \\ \sqrt{m_2} \end{bmatrix} \tag{126}$$

where $M = m_1 + m_2$.

For $\omega_2^2 = \frac{k}{\mu}$:

$$\begin{bmatrix} -\frac{1}{m_2} & -\frac{1}{\sqrt{m_1 m_2}} \\ -\frac{1}{\sqrt{m_1 m_2}} & -\frac{k}{m_1} \end{bmatrix} \mathbf{c}^{(2)} = 0 \quad \rightarrow \quad \mathbf{c}^{(2)} = \frac{1}{\sqrt{M}} \begin{bmatrix} \sqrt{m_2} \\ -\sqrt{m_1} \end{bmatrix} \tag{127}$$

Writing the modes as :

$$Q_n = \sum_i c_i^{(n)} q_i \tag{128}$$
$$= \sum_i c_i^{(n)} \sqrt{m_i} x_i \tag{129}$$

we find:

$$Q_1 = \frac{1}{\sqrt{M}} [\sqrt{m_1}\sqrt{m_1} x_1 + \sqrt{m_2}\sqrt{m_2} x_2]$$
$$= \frac{1}{\sqrt{M}} [m_1 x_1 + m_2 x_2]$$
$$Q_2 = \frac{1}{\sqrt{M}} [\sqrt{m_2}\sqrt{m_1} x_1 - \sqrt{m_1}\sqrt{m_2} x_2]$$
$$= \sqrt{\mu}(x_1 - x_2)$$

Thus Q_1 is proportional to the centre-of-mass coordinate, whilst Q_2 corresponds to the relative coordinate. Varying Q_1 shifts the molecule rigidly, whilst varying Q_2 gives rise to pure vibrational motion. Thus we have *derived* the behaviour of the diatomic without assuming/guessing any knowledge of the likely behaviour. The advantage of this strategy is that it generalises to polyatomics.

C. Generalisation to polyatomics

Consider a molecule consisting of N nuclei, whose cartesian coordinates are denoted by,

$$\mathbf{R} \equiv \{\mathbf{R}_1, \mathbf{R}_2, .., \mathbf{R}_N\} \tag{130}$$

In 3D space, each particle has 3 cartesian coordinates (x, y, z along a lab-fixed frame) , making a total of $3N$ such coordinates. A *potential energy function* $V(\mathbf{R})$ can be assumed to exist which gives the potential energy of the molecule as a function of the particle coordinates.

Let us assume the molecule exists in a stable equilbrium geometry, denoted by $\mathbf{R}^{(0)} = \{\mathbf{R}_1^{(0)}, \mathbf{R}_2^{(0)}, .., \mathbf{R}_N^{(0)}\}$, about which it performs small-amplitude oscillations. It is convenient to define any instantaneous position of the nuclei with reference to the equilibrium geometry, so that

$$\mathbf{R}_i = \mathbf{R}_i^{(0)} + \Delta_i \tag{131}$$

where Δ_i refers to the displacement vector of particle i from the equilibrium position. To make the notation compact in the following few equations, we will refer to the components of the displacement vectors Δ as:

$$\{\underbrace{x_1, x_2, x_3}_{\Delta_1}, \underbrace{x_4, x_5, x_6}_{\Delta_2}, ..., \underbrace{x_{3N-2}, x_{3N-1}, x_{3N}}_{\Delta_N}\} \tag{132}$$

In the equilibrium geometry, the forces on the nuclei vanish, and therefore:

$$\left(\frac{\partial V}{\partial x_i}\right)_0 = 0 \tag{133}$$

The subscript 0 indicates that the derivative is to be evaluated with all $\Delta_i = 0$. Since the nuclei perform small-amplitude oscillations about this equilibrium position, we can Taylor-expand the PE as:

$$V(\mathbf{R}) \;=\; V_0 + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j + \text{ cubic terms } x_i x_j x_k + ... \tag{134}$$

V_0 here denotes the absolute value of the energy of the molecule in its equilibrium geometry. It does not play a further role here, and is important only when comparing energies of different equilibrium geometries (if several exist). In the harmonic approximation, the Taylor series is trucanted after the quadratic terms.

The dynamical matrix, then, is given by:

$$K_{ij} = \frac{1}{\sqrt{m_i m_j}} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \tag{135}$$

$$= \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \tag{136}$$

where, in the second line, we have used mass-weighted coordinates. Diagonalisation of K gives the normal modes, including the rigid translations and rotations. These have frequency $\omega = 0$ associated with them, and are easily identified, the remaining modes being vibrational in character.

D. An example: a triatomic
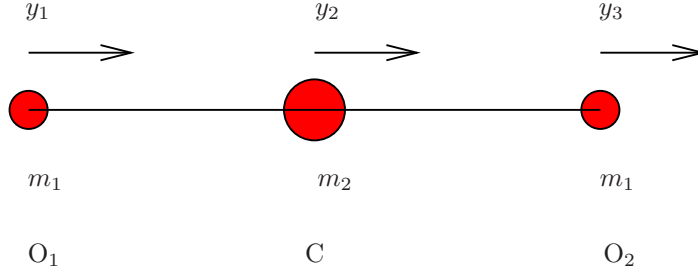
Consider the CO_2 molecule.

FIG. 24: Displacement coordinates for a linear triatomic along the internuclear axis

We will assume that the potential energy function depends quadratically as follows:

$$V = \frac{k}{2} \left((y_1 - y_2)^2 + (y_2 - y_3)^2 \right) \tag{137}$$

If we construct the dynamical matrix K using Eq.(135) we obtain [show!]:

$$
\begin{array}{c|ccc}
 & q_1 & q_2 & q_3 \\
\hline
q_1 & \dfrac{k}{m_1} & -\dfrac{k}{\sqrt{m_1 m_2}} & 0 \\
q_2 & -\dfrac{k}{\sqrt{m_1 m_2}} & \dfrac{2k}{m_2} & -\dfrac{k}{\sqrt{m_1 m_2}} \\
q_3 & 0 & -\dfrac{k}{\sqrt{m_1 m_2}} & \dfrac{k}{m_1}
\end{array}
\tag{138}
$$

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which bears a close resemblence to the Hückel Hamiltonian of a linear chain. Although it can be diagonalised directly, we can use symmtery to simplify the problem, a technique which for larger molecules is indispensible.

Although the point group of CO_2 is $D_{\infty h}$, it is more convenient to construct the character table under a suitable finite subgroup (e.g. C_{2v}), and then to use "descent-in-symmetry" tables to identify the irreps of $D_{\infty h}$. We have:

$$
\begin{array}{c|cccc|c}
C_{2v} & E & C_z & \sigma_{xz} & \sigma_{yz} & \\
\hline
\Gamma_{x_1,x_3} & 2 & 0 & 0 & 2 & A_1 + B_2 \\
\Gamma_{x_2} & 1 & -1 & -1 & 1 & B_2
\end{array}
\tag{139}
$$

i.e.

$$\Gamma_{all} = A_1 + 2B_2 \tag{140}$$

We should therefore expect:

$$A_1 \; : \; 1 \times 1 \text{ Hessian}$$

$$B_2 \; : \; 2 \times 2 \text{ Hessian}$$

Group theory tables tell us $\Gamma_{trans} = \Gamma_y = B_2$, and furthermore, descent-in-symmetry tables tell us the corresponding irreps in $D_{\infty h}$:

$$A_1 \; \rightarrow \; \Sigma_g^+$$

$$B_2 \; \rightarrow \; \Sigma_u^+$$

therefore $\Gamma_{vib} = \Sigma_g^+ + \Sigma_u^+$. Let us see how these arise.

First, construct the symmetry-adapted linear combination of the mass-weighted displacements (by inspection, or more formally, using the projection operator as in Hückel theory):

$$\Sigma_g^+ : \quad \phi_1 \;=\; (q_1 - q_3)/\sqrt{2} \tag{141}$$

$$\Sigma_u^+ : \quad \phi_2 \;=\; q_2 \tag{142}$$

$$\phi_3 \;=\; (q_1 + q_3)/\sqrt{2} \tag{143}$$

The (non-zero) matrix elements of the dynamical matrix in this representation are simply

computed. Eg.:

$$\langle\phi_1|K|\phi_1\rangle = \frac{1}{2}\langle q_1 - q_3|K|q_1 - q_3\rangle = \frac{k}{m_1}$$

$$\langle\phi_2|K|\phi_2\rangle = \langle q_2|K|q_2\rangle = \frac{2k}{m_2}$$

$$\langle\phi_2|K|\phi_3\rangle = \frac{1}{\sqrt{2}}\langle q_2|K|q_1 + q_3\rangle = -\frac{\sqrt{2}k}{\sqrt{m_1 m_2}}$$

$$\langle\phi_3|K|\phi_3\rangle = \frac{1}{2}\langle q_1 + q_3|K|q_1 + q_3\rangle = \frac{k}{m_1}$$

So the Hessian becomes:

	ϕ_1	ϕ_2	ϕ_3
ϕ_1	$\frac{k}{m_1}$	0	0
ϕ_2	0	$\frac{2k}{m_2}$	$-\frac{\sqrt{2}k}{\sqrt{m_1 m_2}}$
ϕ_3	0	$-\frac{\sqrt{2}k}{\sqrt{m_1 m_2}}$	$\frac{k}{m_1}$

(144)

We immediately get one solution

$$\Sigma_g^+ : \quad \lambda_1 = \frac{k}{m_1} \tag{145}$$

which is purely given by $\phi_1 = \frac{1}{\sqrt{2}}(q_1 - q_3) = \sqrt{\frac{m_1}{2}}(x_1 - x_3)$; this is the symmetric stretch with freqency $\omega_1 = \sqrt{k/m_1}$.

The other two solutions with Σ_u^+ symmetry are obtained from:

$$\begin{vmatrix} \frac{2k}{m_2} - \lambda & -\frac{\sqrt{2}k}{\sqrt{m_1 m_2}} \\ -\frac{\sqrt{2}k}{\sqrt{m_1 m_2}} & \frac{k}{m_1} - \lambda \end{vmatrix} = 0$$

$$\left(\frac{2k}{m_2} - \lambda\right)\left(\frac{k}{m_1} - \lambda\right) - \frac{2k^2}{m_1 m_2} = 0$$

$$\lambda^2 - \lambda\left(\frac{2k}{m_2} + \frac{k}{m_1}\right) = 0$$

$$\lambda = \begin{cases} 0 \\ \frac{kM}{m_1 m_2}, & (M = 2m_1 + m_2) \end{cases} \tag{146}$$

$\lambda = 0$ corresponds to the rigid translation of the whole molecule (with $\omega_2 = 0$), whilst the third solution gives the frequency of the anti-symmetric stretch mode, $\omega_3 = \sqrt{kM/(m_1 m_2)}$.

The normal modes can also be easily worked out. We do this for the Σ_u^+ anti-symmetric stretch, which involves finding the appropriate linear combinations of ϕ_2 and ϕ_3. We have

$\omega^2 = \frac{kM}{(m_1 m_2)}$:

$$\begin{bmatrix} \frac{2}{m_2} - \omega^2 & -\frac{\sqrt{2}}{\sqrt{m_1 m_2}} \\ -\frac{\sqrt{2}}{\sqrt{m_1 m_2}} & \frac{1}{m_1} - \omega^2 \end{bmatrix} \mathbf{c}^{(antisym)} = 0$$

$$\begin{bmatrix} \frac{2}{m_2} - \frac{M}{(m_1 m_2)} & -\frac{\sqrt{2}}{\sqrt{m_1 m_2}} \\ -\frac{\sqrt{2}}{\sqrt{m_1 m_2}} & \frac{1}{m_1} - \frac{M}{(m_1 m_2)} \end{bmatrix} \mathbf{c}^{(antisym)} = 0$$

$$\rightarrow \quad \mathbf{c}^{(antisym)} = \frac{1}{\sqrt{M}} \begin{bmatrix} -\sqrt{2m_1} \\ \sqrt{m_2} \end{bmatrix}$$

$$\begin{aligned} Q^{(antisym)} &= \sum_i c_i^{(antisym)} \phi_i \\ &= \frac{1}{\sqrt{M}} \left(-\sqrt{2m_1}\phi_2 + \sqrt{m_2}\phi_3 \right) \\ &= \frac{1}{\sqrt{M}} \left(-\sqrt{2m_1}\cdot\sqrt{m_2}x_2 + \sqrt{m_2}\cdot\sqrt{\frac{m_1}{2}}(x_1 + x_3) \right) \\ &= \sqrt{\frac{\mu}{2}} \left(x_1 - 2x_2 + x_3 \right); \quad \left(\mu = \frac{m_1 m_2}{M} \right) \end{aligned}$$

The Σ_g^+ symmetric stretch normal mode is left as an exercise.

XIII. QUANTUM THEORY OF MOLECULAR VIBRATIONS AND VIBRATIONAL SELECTION RULES

The quantum mechanical theory for molecular vibrations proceeds most easily in terms of the normal-mode coordinates, Q_k, which now take on the form of operators. The corresponding momentum operator p_k, conjugate to Q_k, is $p_k = i\hbar\partial/\partial Q_k$, and in the harmonic approximation, the Hamiltonian operator is expressible as a sum over uncoupled oscillators:

$$H = \sum_i \left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\omega_i^2 Q_i^2 \right) \tag{147}$$

The vibrational wavefunction for the entire molecule factorises into a product of harmonic oscillator states, one for each mode:

$$\Psi_{\nu_1,\nu_2...}(Q_1, Q_2...) = \psi_{\nu_1}(Q_1)\psi_{\nu_2}(Q_2)... \tag{148}$$

(there being $3N - 6$ modes for non-linear molecules and $3N - 5$ for linear ones). When we only want to emphasize the occupation numbers of each mode, we will write the total wavefunction as:

$$\Psi_{\nu_1,\nu_2...} = |\nu_1, \nu_2....\rangle \tag{149}$$

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In this notation, for example, the state in which there is a single excitation in mode i, all other modes being empty, is written as $|0_1, 0_2, ..., 1_i, 0_{i+1}...\rangle$.

The ψ_{ν_i} satisfies the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\omega_i^2 Q_i^2\right)\psi_{\nu_i} = E_{\nu_i}\psi_{\nu_i} \tag{150}$$

with solutions (which you have met in Part IB "Introduction to Quantum Mechanics") expressed in terms of a scaled normal coordinate, y_i:

$$y_i = \sqrt{\frac{\omega_i}{\hbar}}Q_i \tag{151}$$

$$\psi_{\nu_i}(y_i) = C_{\nu_i}H_{\nu_i}(y_i)\exp(-y_i^2/2) \tag{152}$$

where H_ν is a Hermite polynomial, the first few of which are:

$$H_0(y) = 1 \tag{153}$$

$$H_1(y) = 2y \tag{154}$$

$$H_2(y) = 4y^2 - 2 \tag{155}$$

$$H_3(y) = 8y^3 - 12y \tag{156}$$

$C_\nu = (2^\nu \nu! \pi^{1/2})^{-1/2}$ is a normalisation factor. The energy of the νth state of the ith mode, E_{ν_i}, is given by:

$$E_{\nu_i} = (\frac{1}{2} + \nu_i)\hbar\omega_i \tag{157}$$

and the total energy of $\Psi_{\nu_1, \nu_2...}$ is given by:

$$H|\nu_1, \nu_2...\rangle = E_{\nu_1, \nu_2...}|\nu_1, \nu_2...\rangle \tag{158}$$

$$E_{\nu_1, \nu_2...} = \sum_i (\frac{1}{2} + \nu_i)\hbar\omega_i \tag{159}$$

where the sum over i extends over all $3N - 6$ (or $3N - 5$) normal modes of the molecule. The vibrational ground-state, denoted by $|0_1, 0_2, ...\rangle$, with zero quanta in each mode, has the zero-point energy

$$E_{0_1, 0_2, ...} = \sum_i \hbar\omega_i/2 \tag{160}$$

and the ground-state wavefunction has the form:

$$\langle Q_1, Q_2, ...|0_1, 0_2, ...\rangle = C\exp(-\sum_i \omega_i Q_i^2/2\hbar) \tag{161}$$

The symmetry of vibrational wavefunctions can be deduced from the symmetry of the normal mode. Consider a non-degenerate normal-mode Q_i, whose symmetry species is denoted by Γ_i. Q_i^2 transforms as the direct product $\Gamma_i \otimes \Gamma_i = A_1$ (the fully symmetric representation). Therefore the symmetry species Γ_{0_i} of the ground state $\psi_{0_i} \sim \exp(-\omega_i Q_i^2/2\hbar)$ is A_1, and more generally, the n-th excited state $\psi_{n_i} \sim Q_i^n \exp(-\omega_i Q_i/2\hbar)$ transforms as $\Gamma_{n_i} = (\Gamma_i)^{n_i}$. (The first-excited state goes as $\Gamma_{1_i} = \Gamma_i$, the second as $\Gamma_{2_i} = A_1$, etc.)

Concerning the total vibrational wavefunction, we can make similar statements. The ground-state wavefunction given in Eq.(161) contains a sum over squares $\sum_i \omega_i Q_i^2$, where the Q_i do now, in general, include degenerate states. Such sums are invariant under any symmetry operation of the point-group of the molecule. (These operations are orthogonal, and therefore distance-preserving, transformations). The ground-state, therefore, forms a basis for the totally symmetric representation A_1. More generally, the (excited) state $\Psi_{\nu_1,\nu_2..,}$, together with its degenerate partners, form a basis for the (symmetric components of the) representation of $\prod_i \Gamma_i^{\nu_i}$.

A. Selection rules

These results are particularly useful in deciding whether a mode can be spectroscopically active, and whether a transition can be stimulated by electromagnetic (EM) radiation. While the rigorous theory is beyond the scope of this course (we have to deal with the vector potential associated with the electromagnetic field), we will give a approximate account which is sufficient for EM radiation of wavelength long compared to molecular dimensions (e.g. visible light and IR), and which is not very intense. [1] In this case, a molecule placed in an time varying EM field, whose electric-field vector is given by $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$, leads to a perturbation Hamiltonian of the form:

$$H^{(1)} = -\mu.\mathbf{E}(t) \tag{162}$$

---

[1] There are actually other approximations involved as well: taking into account the first-order in the spatial variation in the $\mathbf{E}$-field leads to coupling to the quadrupole operator, and to the magnetic-dipole moment operator, of the system. These terms obey different selection rules to electric-dipole coupling term of Eq.(162), and can induce forbidden transitions. In addition, for a complete theory, one needs to quantize the EM field, rather than assume it to be classical. This is necessary to account the phenomenon of spontaneous emission: in the classical theory, an excited state cannot decay into a lower energy state without the stimulating presence of an EM field.

$\mu = (\mu_x, \mu_y, \mu_z)$ is the 3-component dipole-moment operator of the molecule. In line with the requirement that the EM wave has a very long wavelength, we will take $\mathbf{E}_0$ to be constant (not spatially varying). It is a standard result of time-dependent perturbation theory that the transition intensity between an initial state Ψ_i and a final state Ψ_f is proportional to:

$$I \propto |\langle \Psi_f | \mu.\mathbf{E} | \Psi_i \rangle|^2 = |\mathbf{E}_0.\langle \Psi_f | \mu | \Psi_i \rangle|^2 \qquad (163)$$

Consider the following transition involving an excitation of one mode, say, i:

$$|\nu_1, \nu_2, ...\nu_i...\rangle \rightarrow |\nu_1, \nu_2, ...\nu_i'...\rangle \qquad (164)$$

For this transition to occur, one component of the transition dipole matrix must be non-zero:

$$\langle \nu_1, \nu_2, ...\nu_i...|\mu|\nu_1, \nu_2, ...\nu_i'...\rangle \neq 0 \qquad (165)$$

The integrand transforms as $\Gamma_i^{\nu_i} \otimes \Gamma(\mu) \otimes \Gamma_i^{\nu_i'}$, where $\Gamma(\mu) = \Gamma(x, y, z)$ are the irreps spanned by the Cartesian axes. In the case of the so-called "fundamental" transition, i.e. ($\nu_i = 0 \rightarrow 1$), we must have that $\Gamma_i \otimes \Gamma(\mu) \supset A_1$. (This means that $\Gamma_i \otimes \Gamma(\mu)$ must contain A_1). This forms the basis for the well-known rule that modes which are IR active transform as a component of μ.

Raman activity depends on the matrix elements of the polarisability[2] tensor α, i.e. $\langle \nu_i | \alpha | \nu_i' \rangle$, and hence on whether irreps spanned by the integrand, i.e. $\Gamma_i^{\nu_i} \otimes \Gamma(\alpha) \otimes \Gamma_i^{\nu_i'}$ contain A_1. One can show that $\Gamma(\alpha)$ go as quadratic forms x^2, xy etc, and therefore modes which transform in this manner will have a Raman active fundamental. It also follows that molecules with *inversion symmetry* cannot have modes which are simultaneously IR active and Raman active; for such molecules, modes which are IR active cannot be Raman active, and vice versa, modes which are Raman active cannot be IR active ("rule of mutual exclusion"). This is because the components of μ change sign under the inversion operation, whilst those of α do not, and therefore μ and α cannot span the same irreps.

This analysis can be extended to *combination bands* in spectra, which arise from the simultaneous excitation of two or more normal modes, e.g. $|0_1, 0_2\rangle \rightarrow |1_1, 1_2\rangle$. This transition will be symmetry-allowed if $\Gamma_1 \otimes \Gamma_2 \otimes \Gamma(\mu) \supset A_1$, and can arise even if the fundamentals $\nu_1 = 0 \rightarrow 1$ and $\nu_2 = 0 \rightarrow 1$ are, *on their own*, forbidden.

---

[2] The polarisability gives the linear response of the induced dipole to an electric field: $\mu^{ind} = \alpha.\mathbf{E}$; its components are $\alpha_{ij} = (\partial\mu_i^{ind}/\partial E_j)_0$. For example $\alpha_{zz} = (\partial\mu_z^{ind}/\partial E_z)_0$, and its symmetry species is the same as z^2.

B. Anharmonicity

The Harmonic approximation represents an idealisation of realistic potential energy surfaces: in the Taylor expansion of Eq.(134) we neglect the cubic and higher order terms. These give terms rise to "anharmonicity": the harmomic oscillator wavefunctions which diagonalise the quadratic Hamiltonian do not diagonalize these higher-order interactions, and as a result cease to be exact, stationary, solutions of the Hamiltonian. These higher order terms give rise to interactions between the normal modes, cause mixing between them, and lead to finite lifetimes.

Writing the third order terms in Eq.(134) terms of the normal mode coordinates:

$$V^{(3)} = \frac{1}{3!} \sum_{ijk} \left(\frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k} \right)_0 Q_i Q_j Q_k \tag{166}$$

The anharmonic energy levels can be expressed in powers of $(\frac{1}{2} + \nu_i)$, e.g. for non-degenerate states:

$$E_{\nu_i} = (\frac{1}{2} + \nu_i)\hbar\omega_i - \sum_j (\frac{1}{2} + \nu_i)(\frac{1}{2} + \nu_j)x_{ij} + ... \tag{167}$$

where x_{ij} are anharmonic constants. (For degenerate states, additional terms arise which we will not delve into).

One consequence of the above form, with the presence of off-diagonal x_{ij}, is that the normal modes are clearly no longer independent of each other, and their states can mix (as long as they have the same symmetry, of course). This means, in addition, that in certain circumstances forbidden transitions can aquire quite substantial intensities.

Such mixing is most pronounced if two (or more) levels of the same symmetry are very close in energy in the harmonic approximtion, e.g. if the fundamental transition of one mode is close in energy to an overtone of another. In $^{12}C^{16}O_2$, for example, the Σ_g^+ symmetric stretch $\omega_1 = 1354$ cm^{-1} and whereas the Π_u bending mode $\omega_2 = 673$ cm^{-1}, meaning that the energy difference between the overtone of the latter with the fundamental of the former is only about 8 cm^{-1}.(Note that the overtone of a Π_u mode contains Σ_g^+ by virtue of $(\Pi_u \otimes \Pi_u)_{sym} = \Sigma_g^+ + \Delta_g$).

The perturbation matrix elements are of the form:

$$\left(\frac{\partial V^{(3)}}{\partial Q_1 \partial Q_2^2} \right)_0 \times \langle 0_1, 0_2 | Q_1 Q_2^2 | 1_1, 2_2 \rangle \tag{168}$$

and turn out to be significant ($\sim 52 \text{ cm}^{-1}$ compared to the 8 cm^{-1} difference in energy levels). As a result, the vibrational Raman spectrum shows transitions for both the overtone of the Π_u bending mode and the Σ_g^+ symmetric stretch with similar intensities, whereas the former would normally be forbidden. This type of mixing between an overtone and a fundamental which are close in energy is called a "Fermi resonance".

A final point concerns the behaviour of potential energy surfaces as a function of normal mode coordinates Q_i. In some cases e.g. the symmetric stretch Q_1 of the linear triatomic, the mode is dissociative, which means that $V(Q_1)$ tends to an asymptotic constant for large Q_1, corresponding to the energy of the dissociated fragments. Others, such as the bending mode Q_2 and the antisymmetric stretch Q_3, are non-dissociative, and the potential energy increases without bound. This consideration is obviously important if one is trying to model the potential energy surface, e.g. a Morse potential may be appropriate for the former, but not for the latter.

Problems

Those denoted with ** are quite lengthy problems.

1. (i) Set up and solve *without using symmetry* the Hückel equations for the π system of the allyl radical (a) (C_3H_5), and hence obtain the energy levels and normalised molecular orbitals. Use diagrams to depict your results.

   (ii) Next, using symmetry, write down symmetry-adapted linear combinations of AOs, and use these to set up the Hückel determinant, and hence solve for the MO's and energy levels. Show that you obtain the same result as in (i).
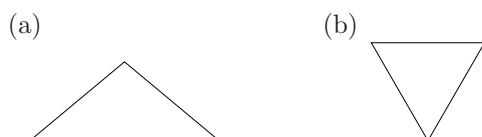

FIG. 25: (a) Allyl radical, (b) Cyclopropenyl

2. Repeat the above exercise for the cyclopropenyl system, (b).

3. (i) Compute the delocalisation energies of cyclobutadiene and butadiene. Are these reasonable values? What effects could further stabilise the cyclic molecule?

   (ii) Assuming that cyclobutadiene undergoes a distortion to a rectangular geometry, let us model this by allowing for two different β's, $\beta_s < \beta_l$. Using the symmetry-adapted orbitals, obtain the energy levels for this system, and hence an expression for the total energy of the distorted molecule. How must the β's vary for a stabilization to occur? Does it depend on the value of β_l?

4. (For the mathematically inclined). Derive the secular equations, Eq.(14), by finding stationary values of the ratio, Eq. (6), with respect to the MO coefficients c_r. [Hint: consider Eq.(13)].

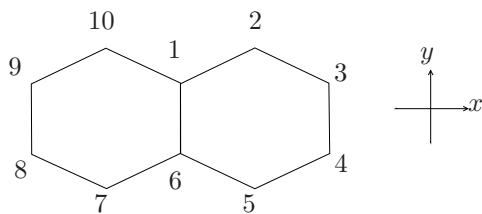5. ** In this question, you will use symmetry to solve for the energy levels and MO's of naphthalene, shown below.

FIG. 26: Naphthalene, and coordinate system to use.

(i)By grouping the AO's which transform into each other under the operations of the point group of the molecule, obtain the irreducible representations spanned by the p_π orbitals, and determine the number and size of each Hückel determinant which arises.

(ii) Set up the symmetry-adapted orbitals for each irreducible representation.

(iii) Using these, setup the four Hückel secular equations, and solve them to obtain the energy levels (labelled by the irreducible representations) given below:

$$
\begin{aligned}
B_{1u}: \quad \epsilon_1 &= \alpha + \beta(1 + \sqrt{13})/2 \approx \alpha + 2.30\beta \\
B_{2g}: \quad \epsilon_2 &= \alpha + \beta(1 + \sqrt{5})/2 \approx \alpha + 1.62\beta \\
B_{3g}: \quad \epsilon_3 &= \alpha - \beta(1 - \sqrt{13})/2 \approx \alpha + 1.30\beta \\
B_{1u}: \quad \epsilon_4 &= \alpha + \beta \\
A_u: \quad \epsilon_5 &= \alpha - \beta(1 - \sqrt{5})/2 \approx \alpha + 0.62\beta \\
B_{2g}: \quad \epsilon_6 &= \alpha + \beta(1 - \sqrt{5})/2 \approx \alpha - 0.62\beta \\
B_{3g}: \quad \epsilon_7 &= \alpha - \beta \\
B_{1u}: \quad \epsilon_8 &= \alpha + \beta(1 - \sqrt{13})/2 \approx \alpha - 1.30\beta \\
A_u: \quad \epsilon_9 &= \alpha - \beta(1 + \sqrt{5})/2 \approx \alpha - 1.62\beta \\
B_{3g}: \quad \epsilon_{10} &= \alpha - \beta(1 + \sqrt{13})/2 \approx \alpha - 2.30\beta
\end{aligned}
$$

Comment on your findings. What is the HOMO-LUMO gap for the neutral molecule?

Compare with the energy levels of the 10-membered cyclic polyene.

(iv) As an optional problem, compute the MO coefficients. Sketch the MOs.

6. Compute the π-populations and bond-orders for the allyl and cyclopropenyl systems (Ques. 1 and 2), including the radicals, the anions and cations. Comment on what you find.

7. Prove that an alternant hydrocarbon with an odd number of electrons must possess a non-bonding orbital. What is the form of this orbital?

8. Azulene (Fig. 7) possesses a large dipole moment. Explain why this might be, and predict its direction.

9. Compute the populations and bond orders in the first (electronically) excited state of butadiene, which consists of the wavefunction $\psi_1^2 \psi_2^1 \psi_3^1$, where $\psi_n \propto \sum_r \sin(\pi n r/5) \phi_r$. Compare the pattern of bond-orders with that of the ground-state [which you need to compute]. What can you conclude about the likely geometry of the 1st excited state, and about the likely reactivity of the terminal sites?

10. Using the MO's tabulated in Table III, evaluate the populations and bond-orders in pyridine, and its cation and anion.

11. Using Hückel orbitals and energies of butadiene, calculate the orbital energies of NC–CN with $\alpha_N = \alpha + \beta/2$ and $\beta_{NC} = \beta$, using perturbation theory. Compare these with the exact Hückel energies $[\alpha + \beta(3 \pm \sqrt{17})/4, \alpha - \beta(1 \pm 5)/4]$, which you should obtain by exploiting symmetry to solve the secular problem.

12. Consider naphthalene as a perturbation of the cyclic 10-membered ring. Using the real orbitals of the latter, evaluate the energy levels of naphthalene using first-order perturbation theory. Take care: you have degenerate levels to think about! Compare your answers with the exact ones evaluated above.

13. ** Use perturbation theory to estimate the bond-orders of naphthalene.

14. ** Use perturbation theory to estimate the π populations on azulene. Where would azulene be preferentially attacked by (a) an electrophile, and (b) a nucleophile?
Use these populations to confirm (or otherwise!) your answer to question 7.

15. By considering pyridine to be a perturbation of benzene with $\alpha_N = \alpha + \beta/2$, compute its π populations using 1st order perturbation theory, and including only the HOMO and LUMO states in this calculation. How good is the result compared to perturbation theory carried out using all the MO's?

16. What are π-populations of the hexatriene molecule? Compute the bond orders, and hence predict the most reactive site for (a) an electrophilic attack , and (b) a nucleophilic attack. [Hint: compute the self-polarisability π_r along the chain.]

17. Construct orbital correlation diagrams for the ring closing of butadiene by both the "disrotatory" and "conrotatory" mechanisms shown below.
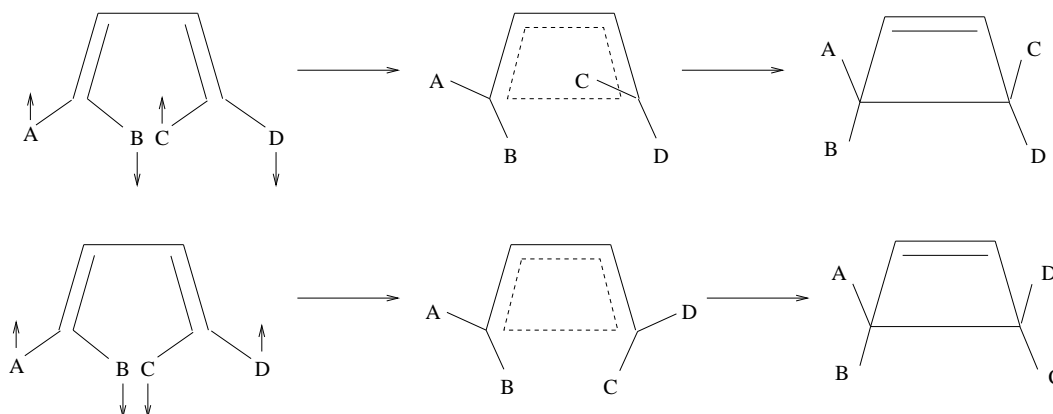

FIG. 27:

18. Verify that the A_{1g} and B_{1u} symmetry adapted linear combinations of the radial displacements for benzene transform in the required manner.

19. ** In section XII.C, we considered the two stretching modes of the CO_2 molecule, i.e.
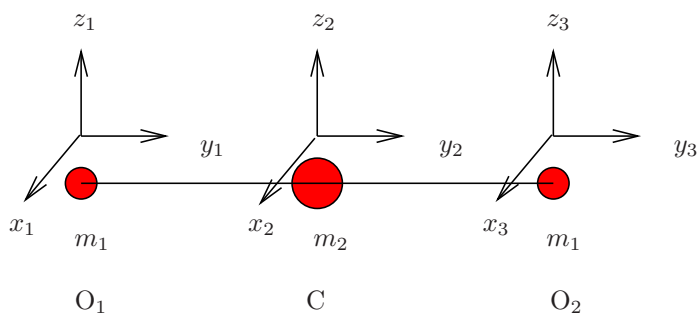

FIG. 28: Cartesian displacement coordinates for a linear triatomic

those modes in which the atomic displacements are confined to the intermolecular axis. In this exercise, we will consider a more general model for CO_2 molecule, which allows for the movement of each atom in three dimensions.

Consider the following interaction model:

$$V(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \frac{k}{2}(R_{12} - R_e)^2 + \frac{k}{2}(R_{23} - R_e)^2 + k'R_e^2 \cos^2(\theta/2) \tag{169}$$

where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$, $R_{ij} = |\mathbf{R}_{ij}|$ is the distance between the atom i and atom j, and θ is the bond-angle between the two interatomic vectors, i.e. given by

$$\cos\theta = \mathbf{R}_{12}.\mathbf{R}_{32}/(R_{12}R_{23}) \tag{170}$$

The equilibrium geometry of the molecule occurs at $R_{12} = R_{23} = R_e$ and $\theta = \pi$. Assume that the molecule is aligned along the y-axis, as shown in the Figure. The last term in V is a bending potential.

Investigate the normal modes of this molecule, using the following steps:

(a) Show that $\Gamma_{vib} = \Pi_u + \Sigma_g^+ + \Sigma_u^+$.

(b) Express the bending potential in terms of $\mathbf{R}_{ij}$ using the identity $2\cos^2\theta = 1 + \cos(2\theta)$.

(c) Show that the second-derivative matrix of the potential with respect to the cartesian components, e.g. $\partial^2 V/\partial y_i \partial y_j$, evaluated at the equilibrium geometry, has the form:

	x_1	x_2	x_3	y_1	y_2	y_3	z_1	z_2	z_3
x_1	$k'/2$	$-k'$	$k'/2$	0	0	0	0	0	0
x_2	$-k'$	$2k'$	$-k'$	0	0	0	0	0	0
x_3	$k'/2$	$-k'$	$k'/2$	0	0	0	0	0	0
y_1	0	0	0	k	$-k$	0	0	0	0
y_2	0	0	0	$-k$	$2k$	k	0	0	0
y_3	0	0	0	0	$-k$	k	0	0	0
z_1	0	0	0	0	0	0	$k'/2$	$-k'$	$k'/2$
z_2	0	0	0	0	0	0	$-k'$	$2k'$	$-k'$
z_3	0	0	0	0	0	0	$k'/2$	$-k'$	$k'/2$

(c) By considering the structure of this matrix, what can you deduce (without doing any calculations) about the normal modes of the molecule?

(d) By forming the (mass-weighted) Hessian matrix show that the bending mode has angular frequency:

$$\omega^{(bend)} = \sqrt{\frac{k'M}{m_1 m_2}}, \quad M = 2m_1 + m_2$$

(e) The vibrational frequencies of CO_2 are: 1354, 673 and 2396 cm^{-1}, the second being the bending mode. Find values for k and k' and comment on your results.

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21. Consider a linear chain of N particles of equal mass m connected by springs of force constant k. The potential is:

$$V(x_1, x_2, ..., x_N) = \frac{k}{2} \sum_i^N (x_i - x_{i+1})^2 \qquad (171)$$

with cyclic boundary conditions $x_{N+1} = x_1$.

Show that the Hessian matrix is:

$$K_{ij} = \frac{2k}{m} \delta_{ij} - \frac{k}{m}(\delta_{j,i+1} + \delta_{j,i-1}) \qquad (172)$$

By noting the similarity with the Hückel ring system, find all normal-modes, and frequencies of this system. Sketch some typical normal modes of this system, noting any characteristic wavelength. How do the vibrational frequencies relate to this wavelength?

22. Which vibrational states of formaldehyde have A_2 symmetry?

23. An overtone transition involves the absorption of two or more quanta in the same mode, e.g. $\nu_i = 0 \rightarrow 2$. Discuss physical mechanisms which allow such transitions to occur.