CH3203 Advanced Physical Chemistry

Molecular Structure and Bonding

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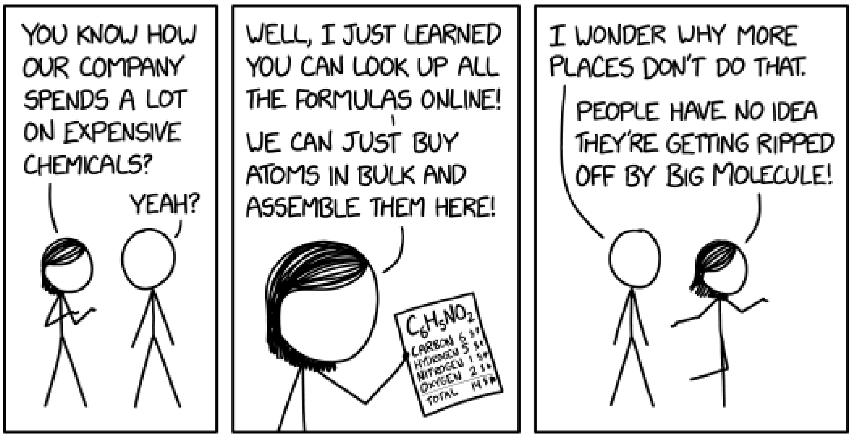

Overview and Introduction

Course Intro

This part of the Advanced Physical Chemistry course is on the topic *molecular structure and bonding*, and forms one third of the module. Naturally, we will take a fairly ‘physical chemistry’ approach to this – it’ll be building on the quantum mechanics we started to learn last year in CH2203, and extending it to larger systems. By the end of the course, we will have seen how we can use applied versions of the quantum mechanics (both on paper and computationally) to predict real chemistry.

Of course, to do this, there is a jump in the complexity of the material (as it’s now *advanced* physical chemistry). However, there is comparatively less material than there was in CH2203, and we will focus on seeing how the stuff *underneath* the examples is all basically the same. We will have 7 lectures and 5 problem sessions (see plan below). The first few lectures are laying some foundation and might seem a bit full of maths – it will lighten up as we get further into the course, I promise.

This course is heavily oriented towards problem solving. The most important resource you’ll have for your revision at the end of this course is your answers to the problems. It will not be enough to just sit through the lectures. **If you can do all the problems without your notes, you will be fine in the exam.**

Really, what you are going to be learning in this course, aside from the chemistry, are two things:

- How to use mathematics to help you solve problems and understand behaviour.
- How to formulate and make complicated scientific arguments.

Both of these skills are much more widely useful than the quantum mechanics is. The QM is just a convenient vehicle we can use to teach you these skills (and is still useful to you as chemists).

Assessment

The course will be assessed by written exam (75%) and by written coursework (if in UoL) or an MCQ (if in DLI) for the remaining 25%. The exam will contain 3 equally weighted questions: one from this part of the course, another from Andrew on spectroscopy, and another from Steve on statistical mechanics.

Required Knowledge

The required knowledge for this course is really everything you’ve learnt up until now. In particular, you’ll need:

- To remember the foundations we laid in the second half of CH2203 (either with me, or with Jake).
- To be comfortable manipulating equations and doing algebra.

There won't be a lot of, if any, calculus in this course. You'll also find it useful to know some basic organic and inorganic chemistry in the later lectures, as we are going to be rationalising some common chemistry you've likely encountered before.

Syllabus and Suggested Reading

These notes are 'complete' in the sense that they define the examinable content. Nothing will be on the exam that isn't in these notes or in the problems. The content in the appendices is there for interest/completeness and will not be examined[1].

However, some of this material is complicated, and you might find other resources useful. Some suggestions would be:

- *Molecular Quantum Mechanics* by Peter Atkins. Goes much further than we need, but contains all the relevant info.
- The Oxford Chemistry Primers on *Quantum Mechanics* (Vol 1 and 2), by Nick Green. Again goes much further in places.

Course Plan

The course will go roughly as follows:

1. Lecture 1. The Variational Theorem.
2. Lecture 2. Secular Equations
3. Lecture 3. MO Theory: Matrix Edition.
4. Problems 1: MO Theory and Matrices.
5. Lecture 4. Hückel Theory I: Foundations.
6. Lecture 5. Hückel Theory II: Applications.
7. Problems 2: Hückel Theory.
8. Extended Problems 1: Hückel Theory.
9. Lecture 6: Electronic Peculiarities.
10. Lecture 7: MO Theory and Symmetry.
11. Problems 3: MO Theory, Symmetry, and Electrons
12. Extended Problems 2: Fun Examples.

There'll also be a session for a piece of practice coursework towards the end.

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[1] Nor will the content of any pithy footnotes - someone asked this in the module feedback last year. Footnotes are just there for fun and to keep me entertained while writing.

Lecture 1

The Variational Theorem

Lecture Aims

- To recap some basics from CH2203.
- To understand **expectation values** and **bra-ket notation**
- To start to understand **The Variational Theorem**.

Last year, we talked about atomic and molecular structure and stopped at the point where we understood the bonding in simple diatomic molecules like H_2 and O_2. Recall that the Schrödinger equation for these molecules isn't analytically solvable, and so we have to make a series of approximations like *The Born-Oppenheimer Approximation* and *The Orbital Approximation* if we want to get anywhere in trying to accurately model molecular structure and energy. This year, we are going to extend this treatment to bigger systems and see how we can understand the bonding in some organic molecules (lectures 4-5) and inorganic molecules (lectures 6-7). Initially though, we need to build up some fundamentals, which is what we'll do in the next three lectures.

1.1 Recap: LCAO Approximation

Recall that the fundamental aim of this whole subject is to find solutions to the time-independent Schrödinger Equation (SE):

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

Solving the SE it really means finding out what the wavefunction, Ψ, is. We usually do this by picking a wavefunction that looks like it will solve the equation, and then optimising it until the solution is as good as we can get. For simple diatomic systems, we built up what we thought was a reasonable wavefunction for the electrons in the molecule (the *molecular orbital*) by adding together wavefunctions for the electrons on the individual atoms (the *atomic orbitals*) – which is known as the **linear combination of atomic orbitals** (LCAO) approach. For something like H_2 where only two atomic orbitals (ϕ) are involved in the bonding, we found that the molecular orbitals (Ψ) were given by:

$$\Psi = c_1\phi_1 + c_2\phi_2 \tag{1.2}$$

The expansion coefficients c_1 and c_2 tell us how much of each atomic orbital ϕ we have in our expansion. In a more general sense, for more than two atomic orbitals, the overall molecular orbital is just given by a sum over the n orbitals we want to use in our expansion:

$$\Psi = \sum_{i=1}^{n} c_i\phi_i \tag{1.3}$$

Remember the set of atomic orbitals[1] we use in our expansion is called the **basis set** for the expansion. It's called this because we use these simpler orbitals as a 'basis' for writing down the more complex molecular orbital. To make an analogy with cooking, the basis set is our list of possible ingredients, and the expansion coefficients tell you how much of each ingredient you need to make your final dish (molecular orbital).

Basis Sets

The **basis set** is the set of simpler functions you use to express a more complicated one. In our case, when a molecular orbital is expressed as a linear combination of atomic orbitals, the atomic orbitals are our basis set.

The more atomic orbitals we use in our basis set, the more flexibility we have to accurately express complex molecular orbitals.

The thing we need to figure out is the value of the **expansion coefficients** in this sum, c_i. So what are they? Last year, in the case of a homonuclear diatomic, we argued via symmetry that $c_1 = \pm c_2 (= c)$ to give us our two molecular orbitals:

$$\Psi^{\pm} = c(\phi_1 \pm \phi_2) \tag{1.4}$$

We get two molecular orbitals (Ψ^+ and Ψ^-) from combining our two atomic orbitals (ϕ_1 and ϕ_2) either in-phase or out-of-phase (have a look back at the CH2203 notes if you need a reminder of how this worked). The approach was based on the electron density in the molecule being the same at all points related by symmetry, but that's not the case for something not symmetrical and homonuclear. We clearly need a more robust way to work out the best expansion coefficients, that is applicable to more systems and more generally.

1.2 Molecular Orbital Energy

We know that atoms in molecules usually want to arrange themselves in such a way that minimises their energy – this is the basis of simple models of molecular structure like VSEPR theory where the distance between electron pairs is maximised to minimise the repulsion and thus minimise the energy of the molecule. We can apply the same argument to finding the best set of coefficients c_i for our LCAO wavefunction: **we want the set of coefficients that minimise the energy of the wavefunction**. So how do we find out the energy[2] of the wavefunction?

1.2.1 Expectation Values

You may think that once we have a wavefunction, Ψ, we just bang it back into the SE (Equation 1.1) to find out the energy. This sounds good, but the problem is that the LCAO wavefunction *is an approximation to the true wavefunction*. The wavefunctions we get via the LCAO approximation don't actually solve the SE, so we can't substitute them back into it and find a single exact energy.

What we can do, however, is find something called the **expectation value** of the energy associated with the wavefunction. **Expectation value** is just a fancy way of saying 'average value', and one of the postulates of quantum mechanics is that the expectation value $\langle O \rangle$ of the observable O that corresponds to the operator $\hat{O}$ is given by:

$$\langle O \rangle = \frac{\int_{\infty} \Psi^* \hat{O} \Psi \, \mathrm{d}\tau}{\int_{\infty} \Psi^* \Psi \, \mathrm{d}\tau} \tag{1.5}$$

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[1] Other kinds of orbital are available.

[2] Or, more strictly, *'the energy of the system described by the wavefunction'*, but saying 'energy of the wavefunction' is less cumbersome.

Where $\mathrm{d}\tau$ means the integral runs over all coordinates of the wavefunction. The mathematical form of this looks a bit intimidating, but don't worry, we aren't actually going to evaluate any of these integrals by hand[3]. Remembering that an integral is really just a continuous sum, you can think of the Equation 1.5 as just saying **'what is the sum of all the possible measurements of observable O my particle could have, weighted by their probability of occurring?'** (see Appendix A for details):

$$\text{Expectation value of } O = \sum(\text{Possible outcomes of } O \times \text{Probability of outcomes occurring})$$

The denominator in Equation 1.5 you may recognise as the normalisation integral we've seen before, and is there to ensure that everything is normalised and that the probabilities behave nicely. As a final note, the notation Ψ^* in Equation 1.5 denotes the *complex conjugate* of the wavefunction Ψ - but again, we don't really need to worry about this for now. In fact, what people who do quantum mechanics normally do is introduce some new notation that neatens this up and de-emphasises the fact that it's an integral[4]. This notation was created by Paul Dirac, and is called **bra-ket** notation.

1.2.2 Bra-ket Notation

In **bra-ket** notation, we write an integral over all space as follows:

$$\int_{\infty} \Psi^* \Psi \, \mathrm{d}\tau = \langle \Psi | \Psi \rangle \tag{1.6}$$

In this notation, $\langle \Psi | \Psi \rangle$ is the called the 'braket', and so $\langle \Psi |$ is the 'bra', and $| \Psi \rangle$ is the 'ket'. How fun.

This notation makes our expression for the expectation value a bit neater:

$$\langle O \rangle = \frac{\int_{\infty} \Psi^* \hat{O} \Psi \mathrm{d}\tau}{\int_{\infty} \Psi^* \Psi \mathrm{d}\tau} = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{1.7}$$

Hopefully you agree that that looks neater. Bras and kets obey a lot of the normal rules of algebra and things that we're used to too, which is nice. We aren't going to do *lots* of work with them in this course, but it'll make it easier to write down some derivations in the coming lectures, and it's useful for you to know about them. If you end up doing anything involving quantum mechanics, spectroscopy, or computational chemistry later in life, you'll encounter them. Let's see a couple of example of where they can neaten things up:

Firstly, we can write down the Schrödinger Equation in bra-ket notation:

$$\hat{H} | \Psi \rangle = E | \Psi \rangle \tag{1.8}$$

This works because the ket $|\Psi\rangle$ is really just a way to represent a quantum state of the system. Knowing that $|\phi\rangle$ or $|n\rangle$ are just different quantum states of a particle or something will go a long way. It's often the case in spectroscopy to see energy level diagrams labelled with $|0\rangle$, $|1\rangle$, $|2\rangle$... for increasing energy levels.

We can also write down the normalisation condition in bra-ket notation. If a wavefunction Ψ is normalised, then:

$$\langle \Psi | \Psi \rangle = 1 \tag{1.9}$$

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[3] Maybe only a very easy case in a problem.

[4] But you do need to remember that in the end it's an integral, all of the things we're doing here are integrals – luckily, computers are really good at doing integrals, so if you've forgotten how to do them by hand, probably no-one will notice.

The overlap integral, S_{12}, between wavefunctions ϕ_1 and ϕ_2 would be:

$$S_{12} = \langle \phi_1 | \phi_2 \rangle \tag{1.10}$$

If two wavefunctions ϕ and ψ are orthogonal (so don't overlap anywhere in space, like a p_x and p_y orbital), then:

$$\langle \psi | \phi \rangle = 0 \tag{1.11}$$

Because the integral ends up being an integral of an odd function over all space – remember that from first year?

Just because we haven't introduced enough new notation, we can summarise all of these integrals as follows:

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Where δ_{ij} is called a **Kronecker Delta**, defined as:

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

In words, this means: *δ_{ij} is 1 if $i = j$, and zero if $i \neq j$'.*

1.2.3 Back to Expectation Values

Anyway, writing down the expression for the quantum mechanical expectation value of an operator is now easy. Let's do it for the most useful operator-observable pair in chemistry: the Hamiltonian operator $\hat{H}$ and the total energy E:

$$\langle E \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{1.12}$$

Our aim is to work out the energy of our molecular orbital Ψ as constructed using the LCAO approximation. Provided we can construct the Hamiltonian (which we did last year), we can use Equation 1.12 to calculate the energy of our orbital. Let's see how this works for the simple homonuclear diatomic case (we saw the result of this last year, but didn't explain how we got there), and then try to extend the result next time to bigger systems. Remember that our molecular orbital was given by:

$$\Psi = c_1\phi_1 + c_2\phi_2 \tag{1.13}$$

The expectation value of the molecular orbital energy is then given by:

$$\begin{aligned}
\langle E \rangle &= \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} && (1.14) \\
&= \frac{\langle c_1\phi_1 + c_2\phi_2 | \hat{H} | c_1\phi_1 + c_2\phi_2 \rangle}{\langle c_1\phi_1 + c_2\phi_2 | c_1\phi_1 + c_2\phi_2 \rangle} && (1.15) \\
&= \frac{c_1^2 \langle \phi_1 | \hat{H} | \phi_1 \rangle + c_2^2 \langle \phi_2 | \hat{H} | \phi_2 \rangle + c_1^* c_2 \langle \phi_1 | \hat{H} | \phi_2 \rangle + c_1 c_2^* \langle \phi_2 | \hat{H} | \phi_1 \rangle}{c_1^2 \langle \phi_1 | \phi_1 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle + c_1^* c_2 \langle \phi_1 | \phi_2 \rangle + c_1 c_2^* \langle \phi_2 | \phi_1 \rangle} && (1.16)
\end{aligned}$$

It looks horrible, but try to work through the above yourself - remember that anything inside a bra gets starred to denote the complex conjugate, and the expansion coefficients c_1 and c_2 can be factored out of the bra-kets, just like a coefficient can be factored out of an integral. We can make the above look a lot nicer if we introduce some simplifying notation and assumptions:

- Let $\langle \phi_i | \hat{H} | \phi_j \rangle = H_{ij}$ (we call this a **matrix element** for reasons that will become clear later).

- Remember the definition of the overlap integral: $\langle \phi_i | \phi_j \rangle = S_{ij}$
- Assume that our basis wavefunctions (atomic orbitals) are normalised, so $\langle \phi_i | \phi_i \rangle = 1$
- Assume that our expansion coefficients are real, so $c_i = c_i^*$.

The expectation value for the energy can then be written as:

$$\langle E \rangle = \frac{c_1^2 H_{11} + c_2^2 H_{22} + c_1 c_2 H_{12} + c_1 c_2 H_{21}}{c_1^2 + c_2^2 + c_1 c_2 S_{12} + c_1 c_2 S_{21}} \tag{1.17}$$

Furthermore, it turns out that $H_{ij} = H_{ji}$ and $S_{ij} = S_{ji}$, due to the properties of the integrals[5]. So, Equation 1.17 becomes:

$$\langle E \rangle = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2 c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2 c_1 c_2 S_{12}} \tag{1.18}$$

That's a bit nicer. Remember that the terms H_{ij} and S_{ij} are just integrals that we can evaluate with a computer, and in the end evaluate to just single numbers. As a teaser for next time, H_{11} and H_{12} are the **Coulomb** and **resonance** integrals that we learnt about at the end of CH2203.

So, have we actually made any progress here? I think we have, even though it might not feel like it. If we look at Equation 1.18, what we've got is an expression for the energy of our molecular orbital $\langle E \rangle$ that is a function of our expansion coefficients c_i, and some integrals H_{ij} and S_{ij}, which are really just numbers because the integral they represent evaluates to just a single number (even if we haven't explicitly calculated that number). The whole point of this exercise was to find out if we can work out the values of our expansion coefficients c_1 and c_2 that minimise the overall energy $\langle E \rangle$. Well, in Equation 1.18 we have an expression for the energy **that is a function of the coefficients**, i.e.:

$$\langle E \rangle = f(c_1, c_2) \tag{1.19}$$

So, if we can vary these coefficients and find the set that give us the lowest energy, we'll have solved our problem. So how do we minimise our function $f(c_1, c_2)$ with respect to the coefficients?

1.3 The Variational Theorem

We learnt how to find the minima and maxima (stationary points) of a function in first year. We had to differentiate the function, set the resulting expression to zero, and solve the resulting equation. In the case here our function has two parameters that we want to minimise, so we actually need to take partial derivatives – one for each parameter – and set them each to zero, but the principle is the same.

If we differentiate our energy with respect to the two expansion coefficients, we'll end up with two equations that we can set to zero and solve simultaneously to find the expansion coefficients that minimise our energy:

$$\begin{aligned} \left(\frac{\partial \langle E \rangle}{\partial c_1} \right)_{c_2} &= 0 \\ \left(\frac{\partial \langle E \rangle}{\partial c_2} \right)_{c_1} &= 0 \end{aligned} \tag{1.20}$$

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[5] And something called the **hermicity** of the operator H, come and ask for details...

We will spend next time talking in much more depth about what this means and how we solve these equations in practice (it is a lot easier than it might seem right now, I promise). However, to end on, there are two questions we could reasonably ask:

1. How do I know I'll actually find a minimum, and not a maximum, or a random saddle point for the energy, after I solve Equation 1.20?
2. Even if I do find a minimum, what if the minimum is actually *lower* in energy than the true ground state?

The first point is easy to answer - we just check the sign of the second derivative like we learnt in first year maths. The second point is more subtle. After all, the LCAO approximation is only approximating the true ground state energy of the system. Couldn't I overshoot in my minimisation and end up with an unphysically low energy?

Helpfully, the answer is **no**, due to something called **The Variational Theorem** (VT). The VT states that:

$$\langle E \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \tag{1.21}$$

Where E_0 is the *true* ground state energy of the molecule. We can prove the VT (see Appendix B), but what it means is that **any energy we calculate using an expectation value will always be greater than or equal to the *true* lowest energy of the system**.

The Variational Theorem

The Variational Theorem states that:

$$\langle E \rangle \geq E_0$$

Where $\langle E \rangle$ is the expectation value of a wavefunction made using the LCAO method, and E_0 is the *true* ground state energy of that molecular orbital. The implication of this is that by minimising $\langle E \rangle$, we will get as close as we possibly can to E_0 – and hence the most accurate wavefunction.

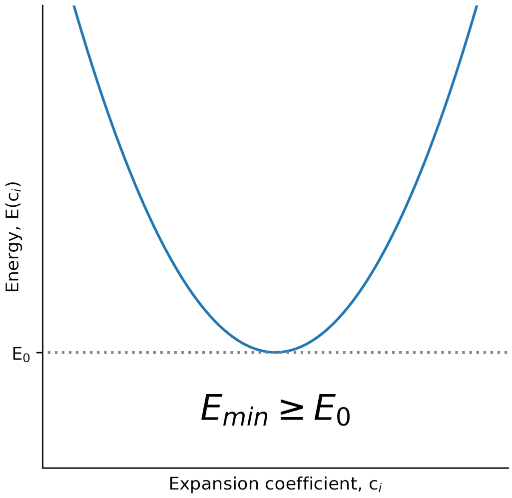

Figure 1.1: Minimising the expectation value of the energy of a system $E(c_i)$ with respect to the expansion coefficients c_i to find a minimised energy E_{min} will never produce an energy that is lower than the true ground state energy, E_0.

The VT is powerful, because it means that we can aggressively optimise our trial LCAO wavefunctions as hard as we want, and we'll never overshoot and end up with an artificially low energy – shown in Figure 1.1. We know, thanks to the VT, that if we keep on decreasing the energy by optimisation and tweaking parameters, that we're always just getting closer and closer to the true solution of the SE.

That was a lot to take in. Next time, we're going to unpack Equation 1.18 a lot more, and show how Equation 1.20 leads to something called **secular equations**. I'm excited.

Take Home Messages

- Our LCAO approach from CH2203 is good, but we need to extend it to larger molecules if it's going to be interesting.
- We can calculate the energy of our LCAO molecular orbital using expectation values - bra-ket notation simplifies writing all this down.
- Our aim is to find the best set of coefficients in the LCAO expansion - the set that minimise the overall energy. The variational theorem shows that by doing this, we'll find the best estimate possible for the true energy of the system.

Lecture 2

Secular Equations

Lecture Aims

- To understand how the variational theorem leads to **Secular Equations**.
- To understand how matrix methods allow us to solve systems of equations like the secular equations.
- To reinforce the methodology we are using, in preparation for applications next time.

Last time we started to figure out a way in which we could make the LCAO approach applicable to larger molecular systems:

- First of all, we found a way to evaluate the energy associated with a given LCAO wavefunction (via the **expectation value**).
- Then we used this to get an expression for the energy $\langle E \rangle$ associated with the wavefunction as a function of the expansion coefficients c_i.
- We then noted that if we could minimise $\langle E \rangle$ with respect to all the different expansion coefficients c_i, that we'd have the best set of expansion coefficients (the ones that give us the wavefunction with the lowest corresponding energy), and thus have the best LCAO wavefunction we can, given our basis set.
- The **variational theorem** told us that this energy would never be lower than the the *true* energy of the ground state, so minimising it is an acceptable strategy.

Today we are going to see what this means for us in our quest to understand molecular structure and bonding.

2.1 Setting up the Problem

If we continue with our simple case where there are just two expansion coefficients, c_1 and c_2, then our energy $\langle E \rangle$ depends on two parameters. Minimising this means we taking the partial derivative of the energy with respect to each parameter, and setting the resulting equations equal to zero, from last time (Equation 1.20):

$$\begin{aligned}\left(\frac{\partial\langle E\rangle}{\partial c_1}\right)_{c_2} &= 0\\ \left(\frac{\partial\langle E\rangle}{\partial c_2}\right)_{c_1} &= 0\end{aligned} \tag{2.1}$$

So, if we evaluate the derivatives we will have two equations (the ones above) and two unknowns (the energy E, and the ratio of the coefficients[1] c_1/c_2). We need to solve the equations simultaneously to find the ratio of the coefficients and energy that corresponds to our lowest energy wavefunction. In problem sheet 1 you will do this by hand, but for now, we are just going to quote the result so we can move forward. After doing derivatives, the two equations we will need to solve are:

$$\begin{aligned}c_1H_{11} + c_2H_{12} - E(c_1 + c_2S_{12}) &= 0\\ c_2H_{22} + c_1H_{21} - E(c_2 + c_1S_{21}) &= 0\end{aligned} \tag{2.2}$$

Where we said last time that the H_{ij} and S_{ij} terms are the Hamiltonian matrix element and overlap integral between atoms i and j respectively. We will identify these with the Coulomb and resonance integrals soon, but for now will leave it as written above.

We could probably solve the equations in Equation 2.2 by hand, but remember that we're trying to find a method that will work for big molecules, and so far we're still working with a diatomic: if we have more atoms, and so more basis functions, we're going to have more coefficients c_i and more partial derivatives to evaluate (Equation 1.20). In turn, this will mean that we have more simultaneous equations to deal with in the end.

In fact, if we have n functions in our basis set, we're going to have n coefficients to optimise and then n simultaneous equations to solve. I can solve two or three simultaneous equations by hand, but what if I had a molecule containing 10, 20, or 100 atoms? We need a way to enable us to solve these simultaneous equations more quickly and efficiently - a method that is scalable to large systems.

2.2 Matrix Methods

Helpfully, the problem of solving large systems of equations with many unknowns is one that humanity has been wrestling with for a couple of thousand years – at least as far back as 200BC, where the first examples of **matrix methods** appeared in the ancient Chinese book 'Nine Chapters on the Mathematical Art' (九章算术). It turns out that being able to solve large numbers of simultaneous equations is very useful if you're trying to work out how to maximise your income from farming, and most of the early work on the technique was motivated by this.

If you're a UoL student you probably haven't heard of matrix methods[2], but you may have done them if you're a student in DLI. We aren't going to go deeply into matrix algebra in this course, but matrices are something which it is important to be aware of if you want to go any further into physical chemistry after this course. All 'real-life' quantum and computational chemistry, and pretty much any other kind of mathematical modelling in any field (finance, drug discovery, engineering...), ultimately boils down to getting computers to manipulate and solve systems of equations using matrices.

A **matrix** in this context is just a word for an array of numbers. Here's an example of a matrix:

$$\begin{pmatrix} a & b\\ c & d\end{pmatrix}$$

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[1] The coefficients are not independent due to normalisation, we can't vary one without changing the other and keep our wavefunction normalised.

[2] Unless you did further maths at A-level.

Figure 2.1: Ancient Chinese mathematician Liu Hui – who wrote about a matrix method now known as *Gaussian Eliminiation* about 1500 years before Gauss did. History is unfair sometimes.

We denote the *matrix* with brackets, and the numbers a, b, c, d are called the *elements* of the matrix. When we talk about matrices we often talk about *rows* and *columns* of the matrix, which should be intuitive.

There are various rules that govern how we can manipulate these arrays of numbers, and I'd direct you to any mathematics textbook for a basic introduction if you'd like to know more[3]. Many problems in the natural sciences are made solvable by casting the problem as a matrix problem. **Matrix algebra**, or **linear algebra**, is the term used to refer the branch of mathematics that concerns matrices[4].

In this course, there are two important things to know about matrices:

1. That we can recast a system of simultaneous equations as a single matrix equation.
2. That this matrix equation will only have a non-trivial solution if the **determinant** of the matrix is zero.

Let's explore these two things now.

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[3] For example, *Foundations of Science Mathematics* by Sivia and Rawlings, or *Engineering Mathematics* by Stroud.

[4] For an introduction to linear algebra, there is no better place to start than 3blue1brown's *'Essence of Linear Algebra'* series: `https://www.3blue1brown.com/topics/linear-algebra`

2.2.1 Simultaneous Equations in Matrix Form

Taking our secular equations from above:

$$\begin{aligned} c_1 H_{11} + c_2 H_{12} - E(c_1 + c_2 S_{12}) = 0 \\ c_2 H_{22} + c_1 H_{21} - E(c_2 + c_1 S_{21}) = 0 \end{aligned}$$

We can rewrite them in a way that collects together the terms that depend on c_1 and the terms that depend on c_2:

$$\begin{aligned} c_1(H_{11} - E) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - E) = 0 \end{aligned} \tag{2.3}$$

Using matrix algebra, we can write these equations as a product of a 2×2 matrix and a 2×1 matrix (or *column vector*):

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{2.4}$$

It's not critical for you to understand how the multiplication of these matrices reproduces the secular equations in this course, but hopefully you can see that there is some similarity between Equation 2.3 and Equation 2.4. If we had more atoms in our basis set, and so more coefficients to optimise with, we would just add rows and columns to these matrices. For example, if I had three atoms to worry about:

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - E & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \tag{2.5}$$

Where I've assumed that all three atoms are the same for simplicity. We can extend this treatment to larger systems: for n atoms (or functions) in our basis set, we will have an $n \times n$ matrix and $n \times 1$ matrix representing our secular equations.

Ok - so, that seems fine. But it's not clear yet how this helps us. Remember that the point of what we are doing here is to work out the set of coefficients c_i that minimise our energy E. How can we use the matrix equation in Equation 2.4 to work out these coefficients, and the associated energies?

2.2.2 Determinants

Solving the set of equations in Equation 2.4 means finding the coefficients c_i (and the associated energy, E) that satisfy the equation. The eagle-eyed among you may realise that one obvious solution is:

$$c_1 = c_2 = 0$$

Or in matrix form:

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

This is called the **trivial solution**, because it's trivial to find (provided you know that $0 \times 0 = 0$). It's also a really boring solution from the point of view of molecular structure, because if $c_1 = c_2 = 0$ then our molecular orbital doesn't exist.

More interesting, is the possiblity of there being **non-trivial solutions**. Sparing some of the detail, a non-trivial solution to a system of equations like that in Equation 2.4 exists when the **determinant** of the $n \times n$ matrix is equal to zero. So what is a determinant?

A **determinant** is a number that you compute from a matrix by following a simple set of rules. Determinants are usually denoted with vertical straight lines as their sides, rather than brackets. The determinant of the 2×2 matrix from earlier:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

Is given by:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

As a concrete example:

$$\begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = 1 \times 4 - 3 \times 2 = 4 - 6 = -2$$

The determinant *is just a number*, but it can tell you all kinds of things about the matrix it was calculated from (beyond the scope of today). We will practice calculating determinants, as it will be used extensively in the next part of this course when we start talking about structures of organic molecules. In this course I am only going to expect you to be able to expand 2 × 2 (as above) and 3 × 3 determinants.

Determinants

A determinant is a **number** that you compute from a **matrix**. The determinant of a 2 × 2 matrix is given by:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Calculating Determinants

2 × 2 determinants are easy to calculate - you just follow the formula:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \tag{2.6}$$

2×2 Determinants

Calculate the determinants of the following matrices:

$$M = \begin{pmatrix} -3 & 4 \\ -2 & 1 \end{pmatrix} \qquad M = \begin{pmatrix} x & x^2 \\ x - 1 & 2 \end{pmatrix}$$

3 × 3 determinants are marginally more complicated, but only marginally. We can just follow another formula:

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix} \tag{2.7}$$

You basically reduce the 3 × 3 determinant into a set of three 2×2 determinants, which we then evaluate using Equation 2.6. The method is called **cofactor expansion** if you want to read about it further. It looks fiddly but as we'll see later, often we end up with lots of zeros in our determinants that make expansion easy.

3×3 Determinants

Calculate the determinant of the following matrix:

$$M = \begin{pmatrix} 2 & 0 & x \\ x & 2x & 1 \\ 0 & 3x & 2 \end{pmatrix}$$

2.2.3 Secular Equations

Anyway, the important thing as far as we are concerned is that for our secular equations to have a non-trivial solution, the determinant of the corresponding $n \times n$ matrix must be zero. Let's see how this works for the matrix in Equation 2.4 (and assume that we have a homonuclear diatomic so $H_{11} = H_{22}$ for simplicity):

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{11} - E \end{vmatrix} = (H_{11} - E)^2 - (H_{12} - ES_{12})^2 = 0$$

If we solve the resulting equation for E, we'll find the energies of the 'best' wavefunctions we can have within the LCAO approximation (the ones that minimise the energy):

$$\begin{aligned} &(H_{11} - E)^2 - (H_{12} - ES_{12})^2 = 0 \\ &(H_{11} - E) = \pm(H_{12} - ES_{12}) \\ &\to E^{\pm} = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}} \end{aligned}$$

We can make this all seem more familiar if we change the notation a bit. Let:

- $H_{11} = \alpha$, the **Coulomb integral**.
- $H_{12} = \beta$, the **resonance integral**.
- $S_{12} = S$, the **overlap integral**

Then we find:

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$$

This result should look familiar from CH2203. We have two energies, E^+ and E^-, because we have two molecular orbitals formed from the overlap of our two atomic orbitals: the bonding and the anti-bonding orbital. But what are the coefficients? Now we have the energies, we can substitute them back into Equation 1.20 to find the coefficients. You'll do this in one of the problem sheets, but you'll find that:

$$c_1 = \pm c_2$$

Which is just as we expected for the homonuclear diatomic case, and the result we saw last year.

So what was the point of all the matrix nonsense? Well, the point is that the matrix method of doing this is *much* more scalable to large problems. As long as we can expand the secular determinants (and this is easy, especially if we have a computer), we can work out the energies of our molecular orbitals, and from there get the coefficients of the atomic orbitals in the LCAO sum.

It may all seem a bit long-winded, but if you trust me that it's useful for today, over the next few sessions we will see how we can utilise these matrix methods to calculate the structure and energies of large organic molecules using something called **Hückel Theory**.

2.3 The Upshot

Now, having encountered a load of new maths and complex looking notation, we have a method that we can use[5] to start to calculate the energies of molecular orbitals from the LCAO method. I appreciate that there was a lot of new stuff in these first two lectures – think of it as the activation barrier that you have to overcome to enjoy the course. The amount of complicated new mathematics dramatically drops after today (but there will be a fair bit of algebra).

I think it's useful now to succinctly recap the methodology we've developed for calculating molecular orbital coefficients and energies:

1. Decide how many atomic orbitals to include in your LCAO **basis set** – more gives more accuracy, but comes at the cost of greater complexity and computational cost (i.e. computational time spent).
2. Form an expression for the molecular orbital Ψ made by the l**inear combination of these atomic orbitals** ϕ: $\Psi = \sum_i c_i \phi_i$. Note that we don't yet know the coefficients.
3. The best set of coefficients we can have is the set where the energy of the molecular orbital is minimised. We can't directly calculate the energy of the molecular orbital from the SE, but we can calculate the **expectation value** of the energy $\langle E \rangle$.
4. Using the expression for the expectation value (Equation 1.12) in conjunction with our LCAO summation, we arrive an expression for the energy of the molecular orbital as a function of the expansion coefficients c_i.
5. Minimising the energy of the molecular orbital with respect to each of the coefficients c_i leads to the **secular equations**. The **variational theorem** ensures that the energy we calculate is never lower than the true ground state energy.
6. Writing the secular equations in matrix form makes the whole method much more scalable to large systems. To find the non-trivial solutions to these equations, we require that the **secular determinant** is equal to zero.
7. Solving the equation that results from setting the secular determinant to zero will give us the energies of the molecular orbitals described by our LCAO sum. We can use these to find the expansion coefficients c_i in each of our molecular orbitals.

Ok. I hope that's somewhat clear, but even if it isn't and it all feels a bit chaotic and stressful (and like a lot of maths), please don't panic. We will see over the next three lectures that actually applying all of these steps in practice is not too difficult, and hopefully by the end of the first half of this course you'll have no problem with it.

Next time, we're going to start looking at how all this can help us in practical, actual, chemical problems. Buckle up.

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[5] Or, we can get a computer to use - nobody has time to do big determinants by hand.

Take Home Messages

- Applying the variational theorem to the LCAO wavefunctions leads to a set of simultaneous equations called **secular equations**.
- The **secular equations** can be expressed in **matrix form**, which makes the problem much more scalable to larger systems.
- The secular equations in matrix form only have a solution if the **secular determinant** is equal to zero.

Lecture 3

MO Theory: Matrix Edition

Lecture Aims

- To understand the meaning of the overlap, Coulomb and resonance integrals.
- To use some of the matrix methods in the context of molecular structure.
- To construct some simple MO diagrams based on the solutions to secular equations.

Today I hope we can all take a breath. Lots of new stuff in the last two lectures, but today we'll mostly be doing easy algebra and drawing pictures. We'll do that classic physical chemistry thing of *'explaining things you already know, but showing you* ***why****'*. We're going to use our result from the last lecture to understand rules like:

- Orbitals of very different energies don't mix (or, *why do we only talk about the outer electrons?*).
- Orbitals of different symmetries don't mix (or, *why don't orthogonal p-orbitals interact?*).
- Electronegativity differences lead to polarity (or, *why do the electrons always end up on the oxygen or fluorine?*).

And some more things. It'll be fun. It might feel a lot like we are just pointlessly explaining things you already knew, but really it is the *journey* that is important here, not the end result. We are going to see how application of mathematics to our problem can illuminate the underlying chemistry – probably the most essential skill for any physical scientist.

3.1 Coulomb, Resonance, and Overlap Integrals

Before we use all our new-found matrix abilities to solve problems in molecular structure, let's just think about the Coulomb, resonance, and overlap integrals (α, β, and S). To recap:

- Coulomb integral: $\alpha = H_{ii} = \langle \phi_i | \hat{H} | \phi_i \rangle$.
- Resonance integral: $\beta = H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$, for $i \neq j$.
- Overlap integral: $S = S_{ij} = \langle \phi_i | \phi_j \rangle$, $S_{ii} = 1$.

It'll be useful to have a conceptual understanding of what these three integrals physically represent, using a diatomic molecule as our model system. **Remember that a definite integral**

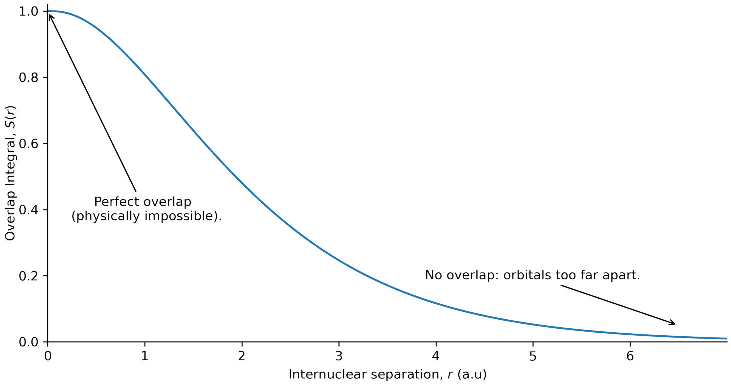

Figure 3.1: Overlap integral as a function of internuclear separation. At zero separation, overlap is perfect ($S = 1$), but this is physically impossible due to nuclear repulsion. As the separation tends to ∞, the overlap tends to zero.

just evaluates to a single number - so you can think of these as just numbers. We'll start with the overlap integral, since that is the simplest.

Overlap Integral

The overlap integral, S, is defined for two orbitals ϕ_i and ϕ_j as:

$$S = \langle \phi_i | \phi_j \rangle = \int_{\infty} \phi_i \phi_j \mathrm{d}\tau$$

In case we needed a reminder that the bra-ket notation referred to an integral. What this physically tells you is the **amount of spatial overlap that there is between the two orbitals.**. If $S = 0$, then there is no overlap, and if $S = 1$ there is perfect overlap. The overlap integral for two s-orbitals is plotted in Figure 3.1. The important points here are:

- The value of the overlap integral is always positive, and lies between 0 and 1.
- The overlap is zero at large separations, as the orbitals are too far apart to interact.
- The overlap is perfect ($S = 1$) at zero separation, but in reality this can't happen because the nuclei would be on top of each other.

The overlap can also be zero if the two orbitals have different symmetry. You know from basic organic chemistry that orthogonal p-orbitals don't interact with each other. This is because the product of those two wavefunctions is an odd function, so the overlap integral is always zero, regardless of the separation.

3.1.1 Coulomb Integral

The Coulomb integral, α, is defined as:

$$\alpha = \langle \phi_i | \hat{H} | \phi_i \rangle$$

If we were to look deeply into the terms from $\hat{H}$ that contribute to this integral, we'd find that we have:

- A term that is just the energy of the orbital ϕ_i on atom i.

- A term that is the energy of attraction of the electron density on atom i to a neighbouring nucleus.
- A term that is the energy of repulsion between adjacent nuclei.

The total Coulomb integral α is the sum of all of these terms. Overall, **think of the Coulomb integral as the energy of an electron on its own atom, but in the presence of a neighbouring atom**.

3.1.2 Resonance Integral

The resonance integral, β is defined as:

$$\beta = \langle \phi_i | \hat{H} | \phi_j \rangle$$

You'll also see the same concept called the 'exchange integral' in other sources. Again, if we were to look deeply at the terms from $\hat{H}$ that contribute to this integral, we'd find that we have:

- A term that is the energy of the orbital ϕ_i on atom i, multiplied by the overlap integral S_{ij}.
- A term that is the energy of attraction of the **overlap electron density** between atoms i and j to nucleus i.
- A term that is the energy of repulsion between nuclei of atoms i and j, again scaled by the overlap integral.

Overall, **think of the resonance integral as the energy of the attraction of the overlap electron density to the nuclei.** In a very crude way, you can think of the Coulomb integral describing the energies of electrons *on their own atoms*, and can think of the resonance integral describing the bonding/anti-bonding interactions: interactions between electrons overlapping to various nuclei.

Important Integrals

- **Overlap Integral**: tells you the degree of spatial overlap between two wavefunctions. Is between 0 (no overlap) and 1 (perfect overlap).
- **Coulomb Integral**: tells you the energy of of an electron on its own atom, but in the presence of a neighbouring atom.
- **Resonance Integral**: tells you the energy of interaction between the overlap electron density between two atoms and their nuclei.

3.2 Diatomic MO Diagrams

We are now in a position to actually explore some chemistry using all the maths we've done up until now. Let's work out MO energies for a generic diatomic molecule. We won't explicitly calculate the wavefunctions, as the energies tell us most of the useful stuff at this stage.

To do this, we are going to work with the secular equations we already constructed in Equation 2.4. Let's re-write these equations using the new notation:

$$\begin{pmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{3.1}$$

I've called the Coulomb integrals α_1 and α_2 because we don't *necessarily* have the same atom now[1]. Let's work out the non-trivial solutions to Equation 3.1 by calculating the secular determinant. After a bit of fiddling, we'll find:

$$\alpha_1\alpha_2 - E(\alpha_2+\alpha_1) + E^2 = \beta^2 - 2\beta ES + E^2S^2$$

Which can recognise is a quadratic equation in E. Rearranging to show this:

$$E^2(1-S^2) + E(2\beta S - \alpha_1 - \alpha_2) + (\alpha_1\alpha_2 - \beta^2) = 0$$

Nice. We can find the solutions (and hence the energies of our system) using the quadratic formula:

$$E^{\pm} = \frac{\alpha_1 + \alpha_2 - 2\beta S \pm \sqrt{(2\beta S - \alpha_2 - \alpha_1)^2 - 4(1-S^2)(\alpha_1\alpha_2 - \beta^2)}}{2(1-S^2)} \tag{3.2}$$

Great - we have two solutions for MO energy (due to the ± in the quadratic formula), which we expect, as we overlapped two atomic orbitals. So where do we go from here? Realistically, we'd stick it into a computer (later), but a good strategy when faced with an intimidating looking equation is to think of some limiting cases, and check that they do what you expect.

3.2.1 Homonuclear case, no overlap

The easiest thing to do first is to check that this equation reproduces some familiar results if we:

- Assume $\alpha_1 = \alpha_2$ (homonuclear).
- Assume $S = 0$ (unrealistic, but gives a decent general guide).

Making these two approximations, Equation 3.2 reduces to:

$$E = \alpha \pm \beta \tag{3.3}$$

Algebra Practice I

Verify that Equation 3.2 reduces to Equation 3.3 when $\alpha_1 = \alpha_2$ and $S = 0$.

That's nice, as it's the behaviour we expect, right? We get two molecular orbitals, with energy $\alpha + \beta$ and $\alpha - \beta$. We can draw this on an MO diagram. Drawing these diagrams is easy once you know a few simple things:

- In the middle of the diagram are the molecular orbitals. At the edges are the atomic orbitals we are overlapping.
- Solid horizontal lines represent energies of atomic orbitals (at the edges) or molecular orbitals (in the middle).
- Conventionally, dashed lines connect the atomic orbitals to the molecular orbitals they produce, but this isn't universal.
- Energy increases from bottom to top, so the lowest orbital drawn is the lowest energy.

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[1] But β will be the same because the interaction of atom 1 with atom 2 is the same as the interaction of atom 2 with atom 1.

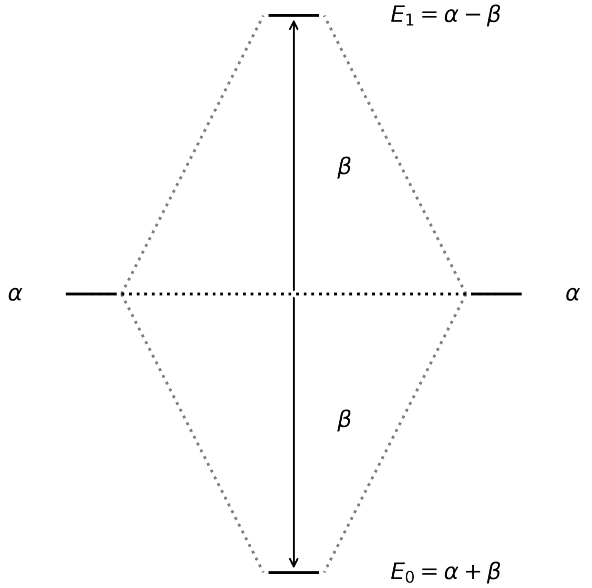

Figure 3.2: MO diagram for a homonuclear diatomic, with $S = 0$. Note that the bonding and anti-bonding orbitals are equidistant from the non-bonding level.

- In this course, we'll call our lowest energy state E_0, and then number them sequentially from there in order of increasing energy.

In Figure 3.2 we have also annotated the difference between the non-bonding level (the average energy of the two atomic orbitals in the absence of bonding, here just $\frac{\alpha+\alpha}{2} = \alpha$). This difference is β, as Equation 3.3 told us. There are some other points worth mentioning about the diagram in Figure 3.2 before we carry on:

- Note that β is a negative number[2], so $\alpha + \beta$ is actually a lower energy than $\alpha - \beta$ (in case anyone thought that was a typo).
- Note that *in the absence of overlap* ($S = 0$), the bonding and anti-bonding MOs are equidistant from the non-bonding level. In other words, the bonding orbital is as strongly 'bonding' as the anti-bonding orbital is 'anti-bonding'.

As we saw last year, this diagram can be used to rationalise things like the bond order of H_2 and other massively relevant systems. Let's continue.

3.2.2 Heteronuclear case, no overlap

The next simplest case, in my view, is to consider the case where we have a heteronuclear diatomic but still ignore overlap, i.e:

- Let α_1 and α_2 be different.
- Still let $S = 0$.

---

[2] A stabilising interaction, reducing the overall energy.

With these approxmations, Equation 3.2 becomes:

$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \frac{\sqrt{(\alpha_1 - \alpha_2)^2 + 4\beta^2}}{2} \tag{3.4}$$

Algebra Practice II

Verify that Equation 3.2 reduces to Equation 3.4 when $\alpha_1 \neq \alpha_2$ and $S = 0$.

This is harder to plot straight away, because we don't know how big the difference in energy between α_1 and α_2 is. We already know that in the case where $\alpha_1 = \alpha_2$ we reduce to the homonuclear case above (Figure 3.2). What about when there's a very big difference in energy between α_1 and α_2?

Limiting case: big energy difference

Let us imagine that the energy gap between the two atomic orbitals (given by $\alpha_1 - \alpha_2$) is much much greater than twice the strength of the bonding interaction between them (given by β):

$$\alpha_1 - \alpha_2 >> 2\beta$$

Meaning:

$$(\alpha_1 - \alpha_2)^2 >> 4\beta^2$$

In this limit, clearly:

$$(\alpha_1 - \alpha_2)^2 + 4\beta^2 \approx (\alpha_1 - \alpha_2)^2$$

Because a massive number plus a smaller number is still a massive number. So the square root in Equation 3.4 becomes:

$$\sqrt{(\alpha_1 - \alpha_2)^2 + 4\beta^2} \approx \sqrt{(\alpha_1 - \alpha_2)^2} = \alpha_1 - \alpha_2$$

If we put this back into Equation 3.4, we find that:

$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \frac{\alpha_1 - \alpha_2}{2}$$

If we explicitly now try to calculate the energies of our two molecular orbitals, we just find:

$$E_0 = \alpha_1 \qquad \text{and} \qquad E_1 = \alpha_2$$

In words: the energies of the molecular orbitals are just the energies of the atomic orbitals, so there's no bonding! This is the basis of the rule that **atomic orbitals of very different energies do not mix**[3].

Limiting case: $\alpha_1 - \alpha_2 = 2\beta$

We can also draw the MO diagram for the heteronuclear case, but we have to assume something about the energy separation of our two atomic orbitals. For the sake of ease, let's assume that:

$$\alpha_1 - \alpha_2 = 2\beta$$

Remember $\beta < 0$, meaning that $\alpha_1 < \alpha_2$. In this limit, Equation 3.4 becomes

$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \sqrt{2}\beta \tag{3.5}$$

Algebra Practice III

Verify that Equation 3.4 reduces to Equation 3.5 in the limit that $\alpha_1 - \alpha_2 = 2\beta$.

Again two molecular orbitals, let's draw the diagram. There are a few noteworthy things in

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[3] Which, if you had forgotten, is why you don't worry about core 1s orbitals when you talk about structures of organic molecules, and other things.

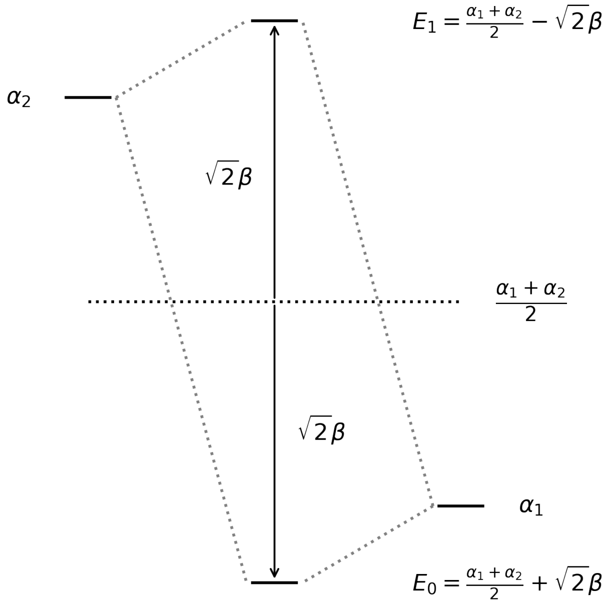

Figure 3.3: MO diagram for a heteronuclear diatomic, with $S = 0$. Note now that the bonding MO is closer in energy to α_1 (the lower energy AO), and the anti-bonding MO is closer in energy to α_2 (the higher energy MO)

Figure 3.3:

- The 'non-bonding' level is now between α_1 and α_2 - it's just the average value of them ($\frac{\alpha_1+\alpha_2}{2}$).
- The two MOs are still equidistant from the non-bonding level.
- The lower energy MO is closer in energy to the lower energy AO, and similar for the higher energy. This means that the bonding MO has more α_1 character than it does α_2.

We can also imagine that as the energy gap between α_1 and α_2 grows, difference in energy between the MOs and their nearest AO drops, as discussed above. Perhaps I'll make a cool animation of that if I have time, but given it's 5.30pm and 33 degrees in my office at the moment, I'm probably going to go to the pub.

3.2.3 Including Overlap

Up until now we've neglected overlap, but that is about to change. Leaving in the overlap makes the algebra a bit more fiddly (but not so much that it's not worth having a go at it[4]). Let's do the homonuclear case with overlap first.

In this case, we'd find that our MOs are given by:

$$E = \frac{\alpha \pm \beta}{1 \pm S} \tag{3.6}$$

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[4] He says optimistically.

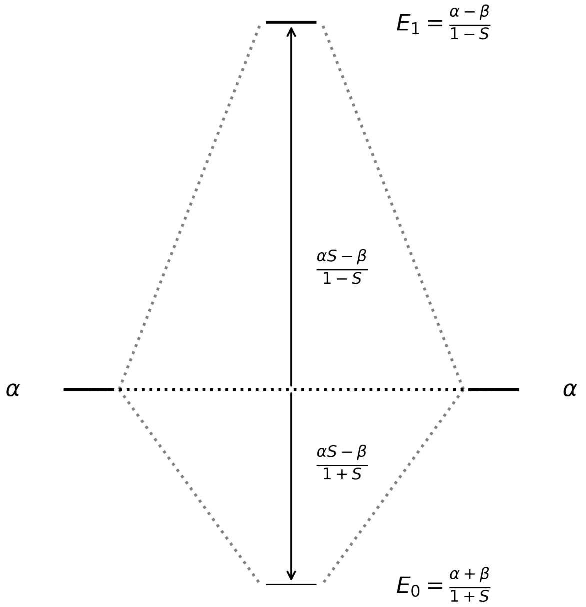

Figure 3.4: MO diagram for a homonuclear molecule, including the effect of overlap. The overlap causes the bonding orbitals to become less bonding, and the anti-bonding orbitals to become more anti-bonding.

Algebra Practice IV

Verify that Equation 3.2 reduces to Equation 3.6 when $\alpha_1 = \alpha_2 = \alpha$ and $S \neq 0$.

Which looks pretty much the same as Equation 3.3, just with an extra factor in the denominator. However, this factor makes a lot of difference to the chemistry. To illustrate this, let's assume that $S = 0.5$. Then our two MOs are given by:

$$E = \frac{\alpha \pm \beta}{1 \pm 0.5}$$

$$\rightarrow E_0 = \frac{\alpha + \beta}{1.5} = \frac{2}{3}(\alpha + \beta) \qquad \text{and} \qquad E_1 = \frac{\alpha - \beta}{0.5} = 2(\alpha - \beta)$$

So, the energy of our bonding MO is only $^2/_3$ what it was in the absence of overlap, but the energy of our anti-bonding MO is double what it was in the absence of overlap! In other words: **the anti-bonding orbitals are more anti-bonding than the bonding orbitals are bonding**. This is shown in Figure 3.4.

We can do a completely analogous analysis with the heteronuclear case. It's just fiddly to do the algebra and easier to just do it on a computer - the result is the same though, anti-bonding orbitals become more anti-bonding, and bonding orbitals become more bonding.

3.2.4 Wavefunctions

We've neglected to mention the wavefunctions for most of today. Recall that in our secular equations we get both energies (which we have discussed *ad nauseam*), and the ratio(s) between different LCAO coefficients. We could take the energies we've got and use them to calculate the ratios (please try!), but actually for the purposes of this course we don't need to get too worried about them. There are just a few points it's important to know:

- The *magnitude* of an LCAO coefficient tells you how much of that AO there is in the overall MO.
- The *sign* of an LCAO coefficient tells you about the phase of the AO (important later on when we start messing around with p-orbitals).
- An AO that is closer in energy to a specific MO will contribute more strongly (bigger magnitude of the coefficient) to that MO. For example, in the heteronuclear diatomic diagram (Figure 3.3), the coefficient of AO 1 in the bonding MO will be bigger than the coefficient of AO 2 (more AO 1 character).
- The square of an LCAO coefficient of a particular atom gives you a measure of the electron density on that atom in a given MO. We will see this again later.

3.3 Applications to Chemistry

It's probably time we bought this back to some actual chemistry. So let's explain some chemical phenomena using the stuff we've just figured out. Our models above were just for two orbitals overlapping, but the results are generalisable to bigger systems.

3.3.1 Dipole Moments and Electronegativity

Question: Can our heteronuclear diatomic MO diagram explain the existence of dipole moments?

A more electronegative atom holds onto its electrons more tightly. In more rigorous language, this means that the energy of the corresponding orbital is lower (lower energy = tightly held = more stable). Look our heteronuclear MO diagram (Figure 3.3). The lowest energy AO is α_1, and the energy of the bonding MO is much nearer α_1. **So we'd expect that the bonding MO has much more $\boldsymbol{\alpha_1}$ character than $\boldsymbol{\alpha_2}$ character**.

If you work out the corresponding LCAO coefficients, this is exactly what you find: $c_1 > c_2$. Remember that the square of the coefficient is proportional to the electron density ρ, so if $c_1 > c_2$, then $\rho_1 > \rho_2$. In words: atom 1 has more electron density on it than atom 2. **This is the essence of polarity** – some atoms holding electrons more tightly than others, creating unequal distributions of charge across the molecule. Quantum mechanics can predict that dipoles exist – neat.

3.3.2 Monatomic Noble Gases

Question: The Noble gases all exist as monatomic species (Ar, He, Ne), not as polyatomic species (like $\mathbf{H_2, O_2, F_2}$). Why is this?

Easy to explain using Figure 3.4, taking Helium as as model case. If we imagined we had He_2 and populated these diagrams with four electrons (two from each helium), we find that the energy of the overall molecular system is:

$$\begin{aligned} E(\mathrm{He}_2) &= 2E_{\text{bonding}} + 2E_{\text{anti-bonding}} \\ &= 2\left(\frac{\alpha+\beta}{1+S}\right) + 2\left(\frac{\alpha-\beta}{1-S}\right) = \frac{4\alpha - 4\beta S}{1-S^2} \end{aligned}$$

The important thing for bonding is the relative stability of this relative to two atoms of unbound Helium, which is:

$$E(2\,\mathrm{He}) = 2\alpha + 2\alpha = 4\alpha$$

Clearly:

$$\frac{4\alpha - 4\beta S}{1 - S^2} > 4\alpha$$

Because β is negative, and the denominator in the first term is less than one. So actually the energy of He_2 is bigger than the energy of two unbound He atoms. Result: they exist as monatomic gases[5]

That is more than enough for today. Hopefully you can see that just by application of relatively simple algebra following the development of our secular equations, we can start to predict interesting and useful chemistry. However, this was just the start. Over the next few lectures we are going to extend this method to much bigger systems and explain and predict things like:

- The Woodward-Hoffmann Rules.
- The $4n+2$ rule for aromaticity.
- Reactivity and stability of various organic molecules.

Take Home Messages

- Solving the secular equations for a generic heteronuclear diatomic leads to expressions for MO energies.
- We can plot these MO energies alongside the original AO energies in an MO diagram.
- By examining these diagrams in different limiting cases, we can start to get a feel for how the chemistry works.

---

[5] Alright, you can make He_2 at very very low temperature (like, sub 10 K), because of weak dispersion forces. They aren't included in our model. Bite me.

Problem Sheet 1

1. Explain the meaning of the following terms/concepts (as they apply to quantum chemistry):
   - i *Molecular Orbital*
   - ii *Expectation Value*
   - iii *Basis Set*
2. What is meant by *The Variational Theorem*? Why is it useful to us?
3. By expanding the secular determinant for a homonuclear diatomic molecule below, derive an expression for the energies of the molecule, E :

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

   Explain the meaning of the terms α, β, and S.

4. The secular equations for a homonuclear diatomic molecule, neglecting the overlap integral, are:

$$c_1(\alpha - E) + c_2\beta = 0$$
$$c_1\beta + c_2(\alpha - E) = 0$$

   Using your result for the energies from Q3, and the fact that the MOs need to be normalised, to answer the following:
   - i Show that in the bonding MO, $c_1 = c_2$
   - ii Show that in the anti-bonding MO $c_1 = -c_2$
5. (*Harder - the only bit of calculus I'm asking you to do*) The expectation value of the energy of a diatomic molecule is given by (from Equation 1.18):

$$\langle E \rangle = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2H_{12}}{c_1^2 + c_2^2 + 2c_1c_2S_{12}}$$

   You are going to show how taking the partial derivatives of this expression lead to the secular equations.
   - i Make the substitutions for the numerator and denominator:

$$A = c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2H_{12}$$
$$B = c_1^2 + c_2^2 + 2c_1c_2S_{12}$$

   Such that:

$$\langle E \rangle = AB^{-1}$$

   Hence use the product and chain rules to show that:

$$\left(\frac{\partial \langle E \rangle}{\partial c_1}\right)_{c_2} = -AB^{-2}\frac{\partial B}{\partial c_1} + B\frac{\partial A}{\partial c_1}$$

ii Show that:

$$\left(\frac{\partial A}{\partial c_1}\right)_{c_2} = 2c_1 H_{11} + 2c_2 H_{12}$$
$$\left(\frac{\partial B}{\partial c_1}\right)_{c_2} = 2c_1 + 2c_2 S_{12}$$

iii Use the results from the above two parts, and letting $\langle E \rangle = E$ for clarity, to show that when:

$$\left(\frac{\partial \langle E \rangle}{\partial c_1}\right)_{c_2} = 0$$

(i.e. at the minimum energy), then:

$$E(c_1 + c_2 S_{12}) - c_1 H_{11} + c_2 H_{12} = 0$$

Which is one of the two secular equations for this system. The other follows by analogy.

Lecture 4

Hückel Theory I: Foundations

Lecture Aims

- To understand the basis of Hückel Theory.
- To construct MO diagrams and calculate energies of simple organic molecules using Hückel Theory.
- To use Hückel theory rationalise and predict chemical properties and spectra.

Today we are going to use the matrix methods and MO theory we've learnt so far to calculate some things that are actually chemically relevant, using something called Hückel Theory. Hückel Theory allows us to apply the MO theory we've learnt to conjugated organic molecules. We can use it to understand the quantum mechanical basis for:

- Aromaticity and anti-aromaticity.
- Regioselectivity of nucleophilic attack.
- The Woodward-Hoffman rules (if time allows next time).

Today we're going to see how the theory works and lay the foundations.

4.1 Basis of Hückel Theory

4.1.1 Conjugated Polyenes

Last time we saw how we can apply MO theory (via the LCAO approximation) to simple diatomic species. It's a big jump in complexity to go from a homonuclear diatomic to a large organic molecule, but there are a couple of things that work in our favour:

- Big molecules can be symmetrical, and symmetry can simplify these calculations.
- We only really care about the valence orbitals, because these are the ones that do all the bonding and determine structure.

The key thing is the symmetry, and we really require our organic molecules to have some kind of symmetry if we are going to be able to apply simple MO theory (that we can do by hand) to them. **Hückel Theory works by exploiting the symmetry that conjugated polyene**

molecules have. These molecules have extended π electron systems and are planar (Figure 4.1). This symmetry, and the fact that the σ and π electrons have different symmetries and energies, means that we can effectively separate the contribution of the σ bond framework from the π bond framework. So, Hückel theory as we are going to use it in this course is only applicable to planar molecules with extended π systems – but this will still open up a large class of molecules that we can work with on paper[1].

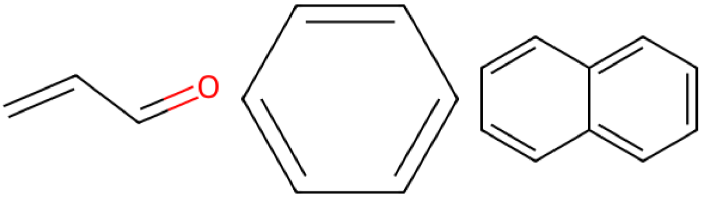

Figure 4.1: Conjugated polyene molecules are the kinds of molecules we can treat using Hückel Theory.

4.1.2 Secular Equations in Hückel Theory

The real trick with Hückel theory is to notice that any conjugated polyene (ethene, benzene, butadiene...) is basically made out of a 'building block' that is an sp^2 hybridised carbon atom with a single electron in the p-orbital - as shown in Figure 4.2. The p-orbital, and hence the whole system of π electrons, is orthogonal to the σ bond framework (so they don't interact), and it's the π framework that we are going to be calculating the energy of using Hückel Theory.

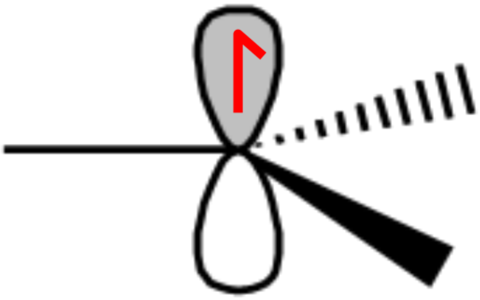

Figure 4.2: An sp^2 hybridised carbon atom is the general building block we use to make molecules in Hückel theory.

We want to build molecules using this building block, and treat them using the secular equations derived previously (Equation 2.4). So, we need to know how to define the matrix elements H_{ij} and S_{ij} within Hückel Theory. These are still going to be defined as Coulomb, resonance, and overlap integrals – but just remember that they're numerically going to be *different* to the ones we had for a simple diatomic like H_2, because the molecule will have a different Hamiltonian. Within Hückel Theory, we say that:

- $H_{ij} = \alpha$ - the Coulomb integral, if $i = j$.
- $H_{ij} = \beta$ - the resonance integral, if $j = i \pm 1$ (i.e. atom i is adjacent to atom j - directly bonded).

---

[1] There are other methods, like *Extended Hückel Theory* that widen this even further - and of course, once you start proper computational chemistry, almost no molecule is too big...

- $\mathrm{H_{ij}} = 0$ otherwise (if atom i is not directly bonded to atom j).
- $\mathrm{S_{ij}} = \delta_{ij}$ - i.e. $\mathrm{S_{ij}} = 1$ if $i = j$, and $\mathrm{S_{ij}} = 0$ if $i \neq j$. Overlap integrals are all zero, except where an atom 'overlaps' with itself.

Assumptions in Hückel Theory

Hückel theory applies to planar, conjugated, polyene molecules. The following assumptions are made:

- The σ and π frameworks of the molecule are separate.
- The molecule can be constructed from building blocks of sp^2 hybridised atoms.
- Each carbon atom contributes one electron to the π system.
- $\mathrm{H_{ij}} = \alpha$ if $i = j$, the Coulomb integral.
- $\mathrm{H_{ij}} = \beta$ if atom i is directly bonded to the neighbouring atom j, the resonance integral.
- $\mathrm{H_{ij}} = 0$ otherwise (for atoms not directly bonded to each other).
- $\mathrm{S_{ij}} = \delta_{ij}$ (overlap integral is zero, except for the overlap of a wavefunction with itself).

4.1.3 Hückel Theory for Ethene

Within Hückel theory, the simplest molecule can make out of our building blocks is ethene - which we get by sticking two of the building blocks together[2]. We can write down the Hückel secular equations for ethene just as we did last time for a diatomic:

$$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{4.1}$$

And we know from before that we need the *secular determinant* to be equal to zero to have a non-trivial solution, so:

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

Expanding this determinant leads to the two MO energies:

$$E = \alpha \pm \beta$$

Remembering that β is negative, the energies in increasing order are:

$$E_0 = \alpha + \beta, \qquad E_1 = \alpha - \beta$$

So, we can draw an MO diagram for the π system of ethene - which would look identical to the one we saw last week in Figure 3.2! But the interesting question to ask here is what the *energy* of an ethene molecule is within Hückel theory - to figure that out, we can draw a simpler diagram which just shows the energies of the MOs. Each carbon atom will contribute one electron to the π system, so in ethene (two carbon atoms) we have two electrons to place in our MO diagram. We populate the electrons from lowest to highest energy, pairing spins as we go. This is shown in Figure 4.3.

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[2] In this way, ethene is like a 'diatomic' molecule within Hückel Theory.

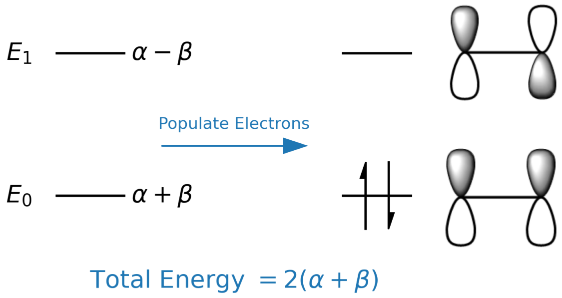

Figure 4.3: Hückel theory applied to ethene. Two MOs are populated with two electrons, the total energy is $2E_0 = 2(\alpha + \beta)$. The corresponding MO wavefunctions Ψ_0 and Ψ_1 are shown on the right hand side.

Figure 4.3 shows that the energy of the π electrons in the ground state of ethene is simply $2E_0$ (as there are two electrons in the E_0 level and none in the E_1 level). The corresponding wavefunctions are shown to the right of the populated MO diagram in Figure 4.3. In this specific case, it's easy to show that:

$$\Psi_0 = c\phi_1 + c\phi_2$$
$$\Psi_1 = c\phi_1 - c\phi_2$$

Simply by analogy with the diatomic case. So in our ground state, Ψ_0, we have no nodal planes, as both AO coefficients have the same sign. In the excited state Ψ_1 there is a nodal plane between the two atoms, as the two AO coefficients have opposite signs.

So what does this tell us? Well, we can work out one useful thing which is the energy of the π bond. The energy of the π bond, E_π must be given by:

$$E_\pi = E_{\text{ethene}} - 2E_{\text{unbonded atom}}$$

i.e. the energy of the π bond is simply the energy of the molecule, minus the contribution to that energy from unbonded atoms. In our notation, this is:

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

So the energy of the π bond is 2β. Recall that β is a negative number[3], typically with a value[4] of around $-100\,\text{kJ mol}^{-1}$. So from our Hückel model, we predict that ethene is stable relative to dissociation into two unbonded atoms, because of the energy of this π bond. To labour the point: the energy of ethene with a π bond is $2\alpha + 2\beta$, and the energy of two unbonded sp^2 hybridised carbon atoms (without a π bond) is 2α. Because $\beta < 0$, ethene is lower in energy than two of these atoms, so we expect it to be stable, which it is.

4.2 Hückel Theory for the Allyl Radical

At this point, some of you are probably thinking:

> *I didn't really need to sit through 4 hours of quantum mechanics to be told that ethene is a molecule that exists.*

---

[3] A π bond being a stabilising thing.

[4] The value varies quite widely depending on the exact molecule you're looking at.

I can understand that viewpoint. So let's do some more interesting things - the next most complicated molecule we can play with after ethene is the allyl radical (CH_2CHCH_2). The first thing we need to do is construct the Hückel secular determinant.

4.2.1 Constructing Hückel Secular Determinants

Constructing Hückel secular determinants is really easy if you're systematic. The best thing to do to start is draw the molecule out and number each atom that contributes to the π bonding framework (here, the three carbon atoms). This is shown for the allyl radical in Figure 4.4. There are three atoms contributing to the π framework here, so we will have a 3 × 3 determinant. The secular determinant will look like this:

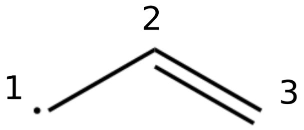

Figure 4.4: The allyl radical, with atoms numbered. Note that this is one of the resonance forms (we will prove later on that it is a delocalised molecule).

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

If you imagine numbering the rows and columns, then there are some simple rules to constructing these:

- Diagonal elements (11, 22, 33...) are all $\alpha - E$.
- Off-diagonal elements where two carbon atoms are directly bonded together (here 12, 21, 23, 32) are β.
- Off-diagonal elements where two carbon atoms aren't directly bonded together (here 13, 31) are 0.

You can now construct these determinants for any conjugated polyene!

Secular Determinant Construction

Construct the 4×4 Hückel secular determinant for butadiene.

4.2.2 Energies of the Allyl Radical

Now we have the secular determinant for the allyl radical, we can expand it, set it equal to zero, and solve to find the energies. We will go through this in the lecture, you should find that:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = (\alpha - E)^3 - 2\beta^2(\alpha - E) = 0$$

Solving this might look like a faff, but we can play a nice trick if we divide the equation through by β^3:

$$\frac{(\alpha - E)^3}{\beta^3} - \frac{2(\alpha - E)}{\beta} = 0$$

And then make the substitution:

$$x = \frac{(\alpha - E)}{\beta}$$

To make the equation:

$$x^3 - 2x = 0$$

This is much more solvable, and you should find that the solutions are:

$$x = 0 \text{ and } x = \pm 2$$

Undoing the substitution will then give us back the three energies of the MO of the allyl cation:

$$\begin{aligned} E_2 &= \alpha - \sqrt{2}\beta \\ E_1 &= \alpha \\ E_0 &= \alpha + \sqrt{2}\beta \end{aligned}$$

We had three AOs to overlap (the three p-orbitals on the three sp^2 hybridised carbon atoms), and thus end up with three MOs. Nice. We can now draw the MO diagram and populate it with the three electrons (LHS of Figure 4.5). We could also work out the LCAO expansion coefficient of each p-orbital and would find that for the three MOs:

$$\begin{aligned} \Psi_2 &= 0.5\phi_1 - 0.71\phi_2 + 0.5\phi_3 \\ \Psi_1 &= 0.71\phi_1 - 0.71\phi_3 \\ \Psi_0 &= 0.5\phi_1 + 0.71\phi_2 + 0.5\phi_3 \end{aligned}$$

These MOs are illustrated on the RHS of Figure 4.5. Note that the changes in sign correspond to a change in the phase of the p-orbital, and the sizes of the p-orbitals reflect the size of the coeffcient.

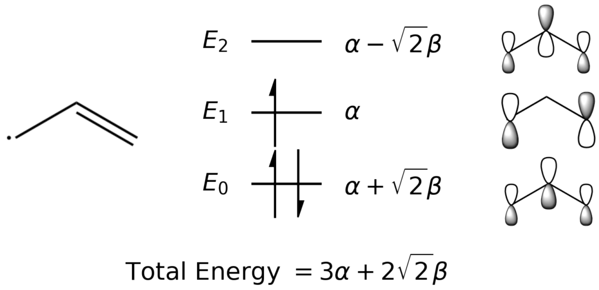

Figure 4.5: Hückel energies and MOs of the allyl radical.

4.3 Chemistry of the Allyl Radical

Now we have those energies, we can do some things with them. First of all, lets answer the question: **is the allyl radical best drawn as a resonance hybrid, or not?**

4.3.1 Allyl Radical Resonance

To do this, we want to compare the energy of a delocalised resonance hybrid with the energy of a non-delocalised equivalent. If the delocalised one is lower in energy, then we know this is more stable. Setting up this calculation is quite easy. First, note that the energy of the delocalised resonance hybrid, E_R is just the total energy of the molecule as calculated by Hückel theory[5]:

$$E_R = 3\alpha + 2\sqrt{2}\beta$$

Then, the energy of the *non-delocalised* variant E_N would just be the energy of a single ethene $(2\alpha + 2\beta)$, plus the energy of a single extra carbon atom (α):

$$E_N = 2\alpha + 2\beta + \alpha = 3\alpha + 2\beta$$

Then, the **delocalisation energy**, E_D, (i.e. the energy difference between the delocalised and non-delocalised version of the molecule) is given by:

$$E_D = E_R - E_N = 3\alpha + 2\sqrt{2}\beta - 3\alpha - 2\beta = 0.82\beta$$

Recall that β is negative, so this means that $E_R < E_N$, and so the delocalised variant is more stable. Thus, we should really draw the allyl radical as as resonance hybrid. Nice to have that confirmed with *maths*.

4.3.2 Electron Densities

Another question we can try to answer is: **what is the electron density on each atom in the molecule?** This is quite easy to calculate from the MO diagram. The electron density on an atom i, ρ_i is given by:

$$\rho_i = \sum n_i c_i^2 \tag{4.2}$$

Where n_i is the number of electrons in an MO (either 0, 1, or 2), and c_i is the coefficient of that atom in that MO, and the sum runs over all occupied orbitals. This equation makes sense if we think about it, because c_i^2 is proportional to the probability of finding an electron on atom i, so really Equation 4.2 says:

$$\text{Electron Density on i} = \sum_{\text{MOs}} (\text{Number of electrons in MO}) \times (\text{Probability of finding electron on i in MO})$$

Doing this calculation for the allyl radical, we'd find:

$$\rho_1 = 2 \times 0.5^2 + 1 \times 0.71^2 + 0 \times 0.5^2 = 1$$
$$\rho_2 = 2 \times 0.71^2 + 1 \times 0^2 + 0 \times (-0.71)^2 = 1$$
$$\rho_3 = 2 \times 0.5^2 + 1 \times (-0.71)^2 + 0 \times (0.5)^2 = 1$$

So, all atoms have equal electron density on them – giving further weight to the idea that this is a delocalised molecule. Neat.

4.3.3 Electronic Spectroscopy

We know from CH2200 last year that the major experimental technique used to verify all this quantum mechanics is spectroscopy. So can we use our simple MO diagram to predict the electronic spectra of the allyl radical?

---

[5] Hückel theory assumes that everything is delocalised.

We can. The first thing to do, though, is to think about what our excited electronic states will be. The ground state will just be lowest energy configuration that we drew in Figure 4.5. We can draw the electrons in different places to make some different excited states, as shown in Figure 4.6. We label the states with kets, the ground state being $|0\rangle$, and the excited states being $|1\rangle, |2\rangle, \ldots$ and so on. All of the excited states shown in Figure 4.6 have been made by moving one electron from the $|0\rangle$ state into a different orbital (spins have not been changed – this is a topic for later).

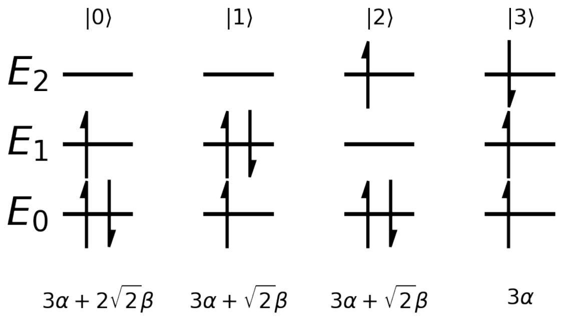

Figure 4.6: Ground state ($|0\rangle$) and three excited states ($|1\rangle, |2\rangle, |3\rangle$) of the allyl radical. Energies of the states calculated from Hückel theory are given below each diagram.

The energy of each state as calculated from Hückel theory is given below each diagram. You should verify these for yourself. If we imagine that we can have a transition between the ground state $|0\rangle$ and any of the three excited states, we can easily calculate the transition energies (and hence, positions of lines in our electronic spectrum) by taking the differences in energy between the upper and lower state:

$$\Delta E(|0\rangle \rightarrow |1\rangle) = (3\alpha + \sqrt{2}\beta) - (3\alpha + 2\sqrt{2}\beta) = -\sqrt{2}\beta$$
$$\Delta E(|0\rangle \rightarrow |2\rangle) = (3\alpha + \sqrt{2}\beta) - (3\alpha + 2\sqrt{2}\beta) = -\sqrt{2}\beta$$
$$\Delta E(|0\rangle \rightarrow |3\rangle) = (3\alpha) - (3\alpha + 2\sqrt{2}\beta) = -2\sqrt{2}\beta$$

Thus, we'd expect to see two lines in our spectrum. β for the allyl radical has a value of around $-200\,\mathrm{kJ\,mol^{-1}}$ ($\approx -2\,\mathrm{eV}$), so the two lines would appear at energies of around 2.8 eV and 5.7 eV (443 and 218 nm). The experimental spectrum shows lines at around these energies[6], which is a nice confirmation that our super-simple model isn't totally nonsensical.

You'll notice that when we drew the excited states in Figure 4.6, we didn't change any of the electron spins. We will see how the spin affects things in two lectures' time, where we will talk

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[6] See *Callear and Lee, Transactions of the Faraday Society, 1967*, or *Aquilante et al. Chemical Physics Letters, 2003.*

in more detail about the orbital symmetry and dig into this a little more deeply. For now though, this is enough - we will explore some more interesting consequences of Hückel theory in the problem sheets and next time.

Take Home Messages

- Hückel Theory is a theory that allows us to apply MO theory to conjugated organic molecules.
- Hückel Theory assumes that the σ and π systems in the molecule are separate and can be treated separately - Hückel Theory calculates the energy of the π system.
- We can use Hückel Theory to predict and explain concepts like delocalisation and resonance (and more next time).

Lecture 5

Hückel Theory II: Applications

Lecture Aims

- To understand how to do Hückel calculations on a computer.
- To understand the basis of the $4n + 2$ rule and *Woodward-Hoffman Rules*.
- To use Hückel theory to explain some organic reactivity.

This lecture is going to be one with a lot of 'doing stuff' on the board. The information below will form the skeleton of what we discuss – but lots of detail will be added in the lecture. A lot of the arguments are going to be easier to explain through drawing and gesticulating than through writing. We may not finish everything in these pages in the lecture, but you'll notice that the two upcoming problem sheets cover many of the same ideas, so we will see them again.

5.1 Hückel Theory on Computers

We're not too worried about doing matrix algebra by hand in this course (although you do need to be able to expand 3 × 3 determinants). Instead, we can use computers to do the hard work for us. There is a very nice, *free*, Hückel calculator called **HuLis**: `http://m.hulis.free.fr/hulis.html`. Using it is pretty self-explanatory, just draw the molecule you want and click 'Results' to see the Hückel energies and MOs. We will use it extensively today.

Of course, if you were inclined to, you could program your own Hückel calculator. **If anyone does this, the person who writes the best one will win an undisclosed prize.**

5.2 Origin of Hückel's Rule

Hückel's rule says that:

- Cyclic molecules with $4n + 2$ π electrons are stable due to **aromaticity**.
- Cyclic molecules with $4n$ π electrons are unstable due to **antiaromaticity**.

Where n is an integer. You should be familiar with these rules from earlier organic chemistry courses. We can explore these rules using the HuLiS calculator. Let's work out the energies of the following species:

- Cyclobutadiene (C_4H_4).

- Benzene (C_6H_6).
- Cyclooctatetraene (C_8H_8).

The $4n+2$ rule tells us that we'd expect benzene to be aromatic (6 π electrons), but that cyclobutadiene and cycloctatetraene should be antiaromatic (4 and 8 π electrons respectively). Calculating the energies, we should find:

$$E(C_4H_4) = 4\alpha + 4\beta$$
$$E(C_6H_6) = 6\alpha + 8\beta$$
$$E(C_8H_8) = 8\alpha + 9.66\beta$$

We can also draw the MO diagram from HuLiS – I'll show this in the lecture. To understand what this tells us, we need to calculate the **delocalisation energy** E_D, as we did for the allyl radical previously. If we repeat the calculation, we'd find that:

$$E_D(C_4H_4) = (4\alpha + 4\beta) - 2(2\alpha + 2\beta) = 0$$
$$E_D(C_6H_6) = (6\alpha + 8\beta) - 3(2\alpha + 2\beta) = 2\beta$$
$$E_D(C_8H_8) = (8\alpha + 9.66\beta) - 4(2\alpha + 2\beta) = 1.66\beta$$

We can interpret this as follows:

- **Cyclobutadiene has the same energy as two isolated ethene molecules**. There is no benefit to it being bonded, and it is very reactive. Furthermore, the MO diagram shows that it has unpaired electrons in it's valence shell – always an indicator of a reactive molecule. **It is antiaromatic and unstable.**
- **Benzene has significantly lower energy (2β) than three isolated ethene molecules**. There are no unpaired electrons in the MO diagram. **Benzene is aromatic and stable.**
- **Cyclooctatetraene (COT) is slightly lower energy (1.66β) than four isolated ethene molecules.** However, it still has unpaired electrons in the ground state making it reactive. COT in reality is not a planar molecule (as Hückel theory assumes), **by distorting away from planar it can remove the antiaromaticity and lower its energy.**

Hopefully you can see here the physical origin of the $4n+2$ rule. You can repeat the same calculation for many molecules (and do some very elegant matrix algebra to show it in a general case, as Hückel did).

Aromaticity and Antiaromaticity

Using the HuLiS calculator and your existing chemical knowledge, explain the physical origin following observations:

- The cyclopentadienyl anion is stable, but the cyclopentadienyl cation is unstable.
- The cyclooctatetraenide dianion is planar.
- Benzene prefers to react via substitution reactions (S_NAr/S_EAr) than via addition reactions.

5.3 Electrophilic Aromatic Substitution

Electrophilic Aromatic Substitution (EAS) reactions are reactions where an electrophile is substituted into an aromatic ring (Figure 5.1). We can use Hückel theory to rationalise the effect of different substituents on the rate of reaction and the regioselectivity of the product.

5.3.1 Rates of EAS

Figure 5.1 shows EAS where a generic electrophile is added to both benzene (top) and phenol (bottom). **Experimentally, it is found that the reaction proceeds much faster for phenol than for benzene**. Why is this?

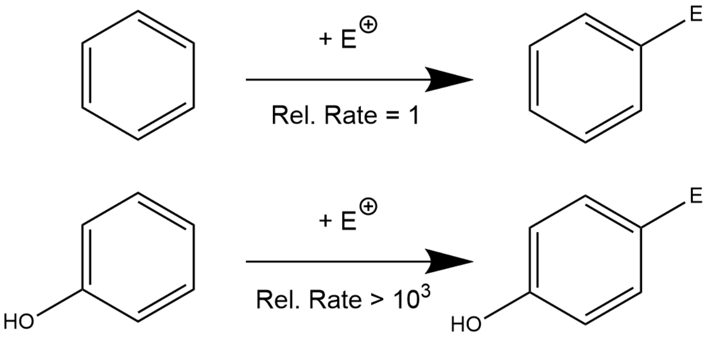

Figure 5.1: Electrophilic aromatic substitution. The rate of reaction is greatly enhanced by addition of an electron-donating group to the ring.

We know that the rate of a chemical reaction is determined by the **activation energy** of the reaction (think back to the Arrhenius equation). The activation energy is the difference in energy between the reactants and the **transition state** of the reaction. In these EAS reactions, electrons leave the aromatic ring and move onto the electrophile. The transition state for this reaction will therefore look approximately like a cationic version of the reactant (Figure 5.2). The activation energy ΔE for these EAS reactions is therefore given approximately by:

$$\begin{aligned}\Delta E &= E_{\text{TS}} - E_{\text{Reactant}} \\ &= E_{\text{ReactantCation}} - E_{\text{Reactant}}\end{aligned}$$

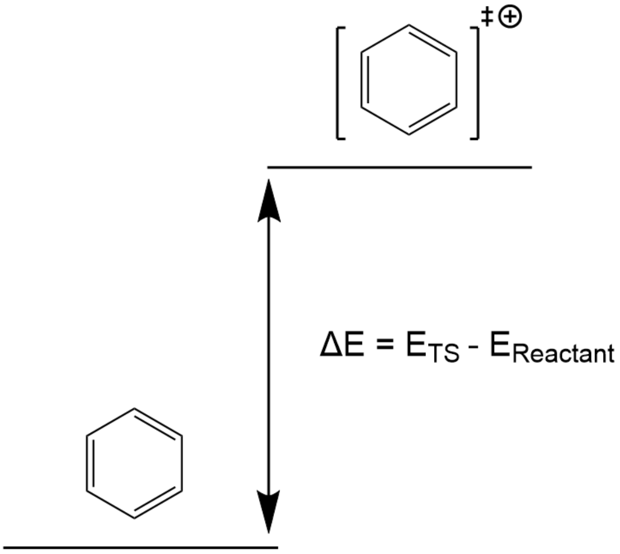

Figure 5.2: The transition state in an EAS reaction will look approximately like a cationic version of the aromatic reactant.

We can calculate approximate energies of both the reactant and cationic TS using Hückel theory.

Let's do this for both benzene and phenol using the HuLiS calculator and see if we can rationalise the difference in rates. These energies are tabulated in Table 5.1.

Reactant	E_{TS}	E_{Reactant}	ΔE
Benzene	$5\alpha + 7\beta$	$6\alpha + 8\beta$	$-(\alpha + \beta)$
Phenol	$7\alpha + 11.43\beta$	$8\alpha + 12.31\beta$	$-(\alpha + 0.88\beta)$

Table 5.1: Energies of the transition state and reactant, and the activation energy for EAS reactions with benzene and phenol, as calculated using Hückel theory.

We can see that the activation energy for EAS on benzene is 0.12β higher than for phenol (remember that α and β are both negative). **Thus we would expect that the EAS rate for phenol is faster than benzene, because the activation energy is lower – so our theory agrees with experiment.**

5.3.2 Directing Effects

That was nice, but we can go a bit further and use Hückel theory to rationalise the directing effect that the phenol substituent will have. We know that as a resonant electron-donating group, the phenol will direct EAS to the ortho and para positions on the ring. You've rationalised this previously in organic chemistry by pushing curly arrows - let's see if quantum mechanics agrees with the curly arrows.

To think about this, we have to think about the molecular orbitals that the electrons are flowing between in our EAS reaction. Clearly, the aromatic ring is putting electrons onto the electrophile, so the transfer of electrons in the reaction must be *from the ring, to the electrophile*. In molecular orbital terms, this means that the orbitals that are involved in our reaction are the HOMO of the aromatic ring and the LUMO of the electrophile[1]. So, we'd expect that the atoms that have the highest electron density on them in the HOMO are the ones where the electrons are most likely to be pushed out from.

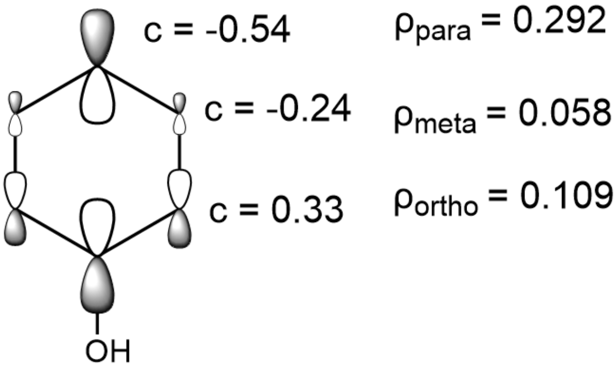

Figure 5.3: The coefficients on each atom in the HOMO of phenol show that the highest electron density is on the para position, then ortho, and then meta. This agrees with the selectivity observed in the EAS product, where we expect that the hydroxyl group is strongly para directing.

To calculate the electron density, we can use the expression for the HOMO from HuLiS, where the AOs in the LCAO sum are numbered clockwise from the carbon with the hydroxyl group.

$$\Psi_{\text{HOMO}} = 0.53\phi_1 + 0.33\phi_2 - 0.24\phi_3 - 0.54\phi_4 - 0.24\phi_5 + 0.33\phi_6$$

---

[1] HOMO = Highest Occupied Molecular Orbital, LUMO = Lowest Unoccupied Molecular Orbital, as a reminder.

This HOMO is sketched out with orbital sizes and phases reflecting these coefficients in Figure 5.3. The electron density ρ on each atom is proportional to the coefficient squared - these densities are written out on the Figure 5.3.

It is clear that the atom with the highest electron density (and thus the most likely to push electrons to an electrophile) is *para* to the hydroxyl group. The ortho position has the next highest electron density, and the meta position has the least. **This correlates exactly with the expectation from curly arrow pushing that EAS would occur first at the para position, then the ortho, and then the meta**. Even a very rudimentary theory like Hückel theory can explain this reactivity!

5.4 Pericyclic Reactions

In organic chemistry this year you've learned (or will learn, if you are in DLI) about **pericyclic reactions**, which are reactions that go via a cyclic transition state without any intermediates. We're going to use Hückel theory to revisit **electrocyclic ring opening/closing**, and look at the effect of substituents on the rates of the **Diels-Alder reaction**.

DLI students: I appreciate that if you've not already learned these concepts in organic chemistry this might be a bit overwhelming. Hopefully it will just lay some foundations that you can revisit later on.

5.4.1 Electrocyclic Ring Opening

Electrocyclic ring opening (or closing) reactions can produce products of two different stereochemistries, depending on if the ring opening is **conrotatory** or **disrotatory**. These options are shown in Figure 5.4. You can select the conrotatory or disrotatory mode by performing the reaction under either thermal (by heating it up) or photochemical (by shining light on it) control, and you decide this via some rules called the **Woodward-Hoffmann** rules. I'm not going to go into what these rules are (you either already know this, or will be taught it later), but I am going to show you how **conservation of orbital symmetry** is what results in these rules.

We will use the ring-opening of cyclobutadiene (shown in Figure 5.4) as an example case, but the same arguments can apply to any similar reaction. The thing I want to to learn here is **how to make these complex scientific arguments** - I don't really care if you can recite the Woodward-Hoffmann rules or not :)

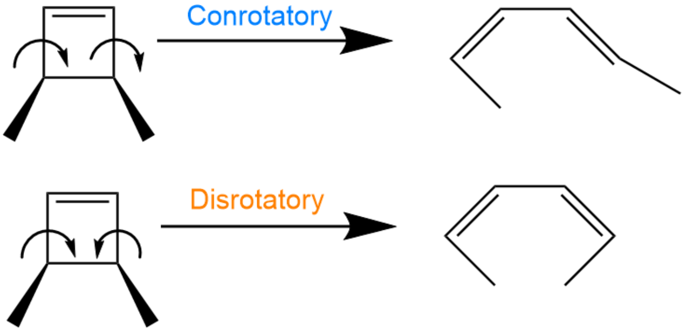

Figure 5.4: Electrocyclic ring opening/closing can be conrotatory (top) or disrotatory (bottom), depending on the way in which the bonds rotate during the reaction. Each path produces products with different stereochemistries.

The first thing we do when analysing a pericyclic reaction like this is to draw out the relevant orbitals. Hückel theory helps us to do this here - and the orbitals of the reactants and products are annotated with phases on Figure 5.6. During the reaction the orbitals of the cyclobutadiene reactant must turn into the orbitals of the butadiene product. We should be able to keep track of how the orbitals change, and **conservation of orbital symmetry** says that the symmetry of the orbitals should be conserved through the reaction: from reactant, to transition state, and to final product[2].

To keep track of this, we need to identify symmetry *elements* of the reactant and product, and any transition states that are conserved during the reaction. The reason these reactions are cool is that the symmetry elements conserved in the transition state are different for the two pathways (Figure 5.5). For our butadiene case:

- In the conrotatory path there is a C_2 rotation axis present in the reactant, product, and transition state.
- In the disrotatory path there is a σ mirror plane present in the reactant, product, and transition state.

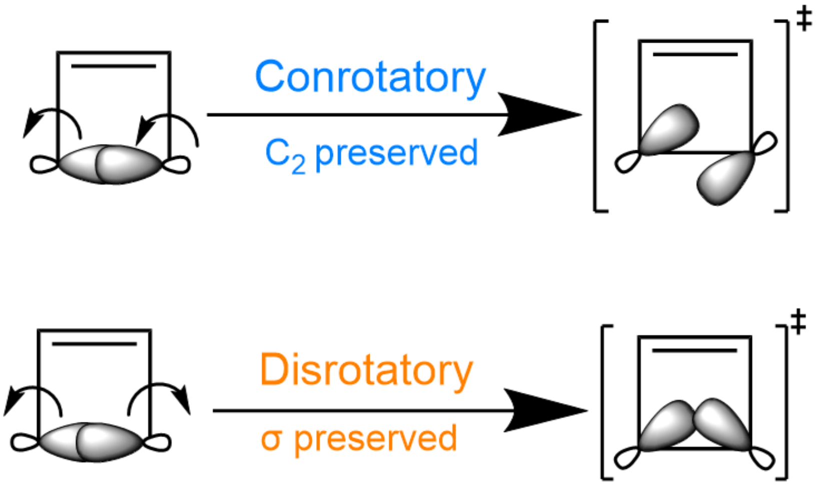

Figure 5.5: Different symmetry elements are preserved in the transition state of the con- and disrotatory pathways.

We can then assess the orbital symmetry conservation by looking at the character of the reactant and product (and TS) MOs under the preserved symmetry element. To conserve orbital symmetry, we must have a **smooth correlation** between reactant, transition state, and product. These correlations are shown for both conrotatory and disrotatory pathways in Figure 5.6 as dashed lines connecting states of the same character (so states that have the same symmetry under the preserved symmetry element). To decide which states of the same character to connect together, we invoke the **non-crossing rule**, which states that **two states of the same symmetry cannot have equal energy**[3].

As an example, looking at Figure 5.6, if I was to connect Ψ_0 in the reactant with Ψ_3 in the conrotatory product side (which have the same character under C_2), I'd have to connect Ψ_2

---

[2] Symmetry actually ultimately results in all of the physical conservation laws we are familiar with (energy, momentum) - see Feynman Lecture 17. Beautiful stuff.

[3] You can show this using the method we looked at in Lecture 3. The energies of two MOs formed from the overlap of two AOs are only equal if $\beta = 0$, which is only true if the symmetry of the two states is different (else there is always a way, albeit possibly small, that the states can mix).

in the reactant to Ψ_1 in the product. The lines connecting these states would cross, implying that these two states have the same energy at some point on the reaction coordinate - but this cannot be true if they have the same symmetry (which they do). So we connect them in the way shown in Figure 5.6.

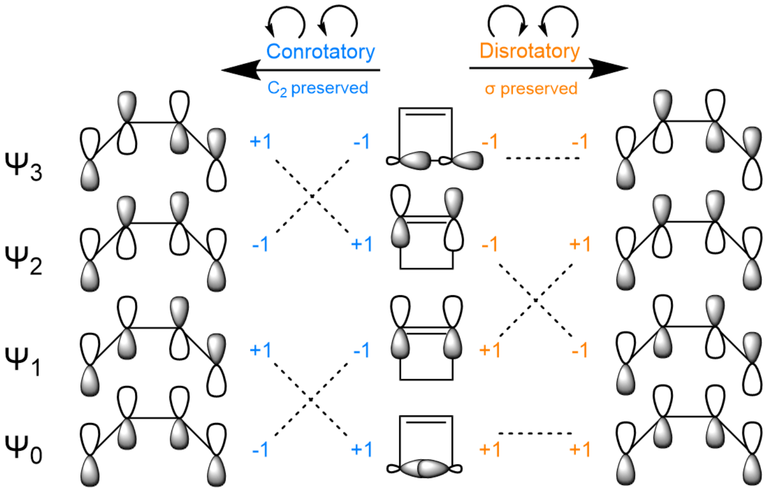

Figure 5.6: Correlation diagram for the electrocyclic ring opening of cyclobutadiene. The MOs of the reactant (middle) and products (edges) are shown in energy order. The conrotatory path is shown on the left and the disrotatory on the right. The character of each MO under the preserved symmetry element in each scheme is annotated next to each MO. Dashed lines join MOs where a smooth correlation (preserved orbital symmetry between reactant, transition state, and ground state) is present.

So anyway, how does this help us predict whether the outcome is allowed or not? To see this, imagine that we have four electrons in the ground state of the reactant, so the electron configuration is $\Psi_0^2\Psi_1^2$. This configuration smoothly correlates (following the dashed lines) with the ground state of the conrotatory product ($\Psi_0^2\Psi_1^2$), and an *excited state* of the disrotatory product ($\Psi_0^2\Psi_2^2$). To form an excited product from a ground state reactant requires a lot of energy, so **from the ground state, the conrotatory product is formed preferentially**.

Conversely, if we had an electronically excited reactant by doing the reaction under photochemical control, our reactant has the configuration $\Psi_0^2\Psi_1^1\Psi_2^1$. This configuration smoothly correlates with the same configuration in the *disrotatory product*, and with a configuration of higher energy ($\Psi_0^2\Psi_1^1\Psi_3^1$) in the conrotatory product. Hence, **from the excited state, the disrotatory product is formed preferentially**.

This argument based on the **conservation of orbital symmetry** is the basis of the Woodward-Hoffmann rules. In fact, conservation of orbital symmetry is such a fundamental physical principle that the Woodward-Hoffmann rules are one of the few sets of rules in organic chemistry that don't have loads of exceptions to them, thanks to quantum mechanics. Nice.

5.4.2 Substituent effects in the Diels-Alder Reaction

The Diels-Alder reaction is a reaction where a diene and a dienophile come together to form a ring. The typical example of a Diels-Alder reaction, with butadiene as the diene and ethene as the dienophile, is shown in the top row of Figure 5.7. Substituents attached to the diene and dienophile have a big impact on the rate of the reaction, as shown in Figure 5.7:

- The rate of reaction **increases** when there is an electron donating group on the diene, and an electron withdrawing group on the dienophile.

- The rate of reaction **decreases** when there is an electron withdrawing group on the dienophile, and an electron donating group on the diene.

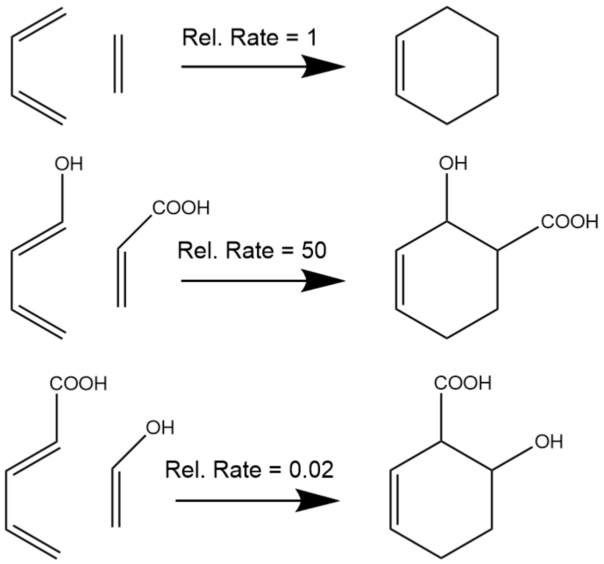

Figure 5.7: Three different Diels-Alder reactions with different electron-donating (OH) and electron-withdrawing (COOH) substituents on the substrates. The relative rates are shown above each reaction arrow.

As the diene and dienophile are prototypical 'Hückel theory' molecules - let's see if Hückel theory can be used to understand these relative rates. The strategy used in the case of EAS above is tricker to apply here, because Hückel theory will struggle to differentiate between the transition states (and because the product formed is not conjugated). However, what we can do is think about the approach of the two reactants and think about which orbitals are interacting.

In a typical Diels-Alder reaction, the diene is electron-rich, and the dienophile is electron-poor. Thus, the orbital overlap that matters in the reaction is between the **HOMO of the diene** and the **LUMO of the dienophile**.

We know from earlier in the course that the more similar the energy of two overlapping orbitals is, the stronger the bonding interaction between them[4]. We'd expect that a stronger interaction between the reactants makes the reaction more favourable and thus faster (you can imagine that the stronger interaction lowers the energy of the resulting transition state - roughly). So, if we can use Hückel theory to look at the energies of the HOMO and LUMO in the three cases above, we should be able to rationalise the relative rates. If we calculate the energies of the HOMO and LUMO for the three sets of reactants shown in Figure 5.7 using Hückel theory, we'd find MO diagrams that look like those shown in Figure 5.8.

We can rationalise the relative rates by looking at the HOMO-LUMO gaps (annotated below each set of diagrams on Figure 5.8:

- The largest HOMO-LUMO gap is for the diene with an EWG and dienophile with an EDG (panel b in Figure 5.8). This reaction is therefore less favourable and has the slowest rate.

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[4] From lecture 3 – compare Figure 3.2 (orbitals with the same energy) and Figure 3.3 (orbitals with different energy). The bonding interaction is strongest (i.e. most different to the non-bonded case) when the energies are similar.

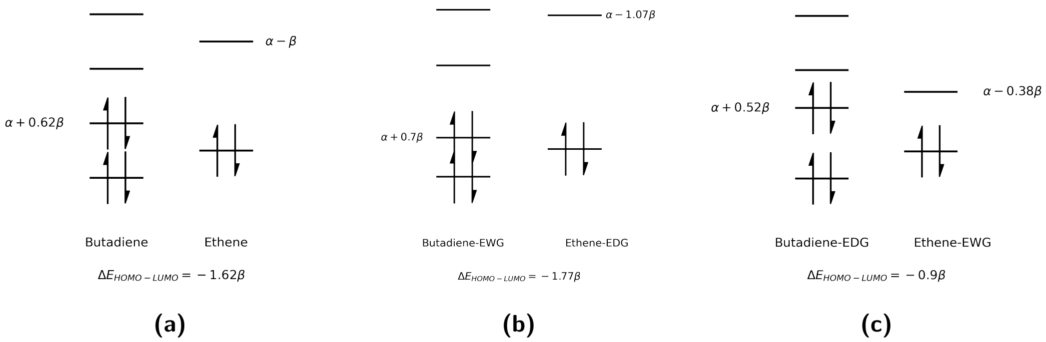


Figure 5.8: MO diagrams for Diels-Alder reactants. (a) ethene and butadiene, (b) with an EDG on the ethene and EWG on the diene, (c) with an EWG on the ethene and EDG on the diene. The energy differences between the HOMO and LUMO in each case explain the relative rates.

- The smallest HOMO-LUMO gap is for the diene with an EDG and dienophile with an EWG (panel c in Figure 5.8). This reaction is therefore more favourable and has the fastest rate.
- The case with 'bare' butadiene and ethene lies between these two extremes.

Remember that the crux of this argument was that the smaller HOMO-LUMO gap leads to a stronger interaction, lowering the energy of the transition state and increasing the reaction rate. Note that in an exam, I would give you the relevant energies and MO diagrams on a question like this (as you won't have access to a Hückel calculator).

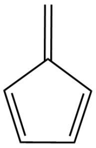
Hopefully by now we can see that application of quantum mechanics (via Hückel theory) to these problems can help us rationalise observed chemistry, and we've seen how to make these quite subtle and complex scientific arguments. That'll be enough Hückel theory for now (except in the problems).Next time, we are going to talk about some complications that arise due to electrons - and understand how to properly label electronic states of molecules.

Take Home Messages

- You can use Hückel energies and wavefunctions to rationalise many reactions in organic chemistry.
- Even this relatively simple and unsophisticated model can qualitatively match experimental observation.
- We've seen how to rationalise structural stability and reaction rates – things that are useful in much wider settings than this course.

Problem Sheet 2

1. Outline the basis of Hückel Theory and how it can be used to calculate energies and wavefunctions for conjugated polyenes. State any simplifying assumptions it makes.
2. Using the energies and MOs for the allyl radical derived in Lecture 4, answer the following questions:
    - i Sketch the three MOs of the allyl radical, indicating any nodal planes on your sketch.
    - ii Calculate the electron density on each atom of the allyl cation. Does the result of this calculation align with how you would draw this cation in organic chemistry?
3. Use the HuLiS calculator to answer these questions about fulvene (below).



    - i Is fulvene an aromatic molecule?
    - ii Sketch the HOMO and LUMO of fulvene.
    - iii Identify the point group of fulvene, and hence the symmetry of the HOMO and LUMO within the point group.
4. Experimentally, it is observed that aromatic molecules preferentially undergo *substitution* reactions, rather than *addition* reactions, which are often very slow.

   Use your knowledge of chemistry, and Hückel Theory, to explain this observation (a calculation may help but is not essential).
5. This question is about the cyclopropene radical (below).

    - i Construct an expand a 3×3 Hückel secular determinant for the cyclopropene radical.
    - ii Show that the MO energies are given by:

$$E_0 = \alpha + 2\beta \text{ and } E_1 = \alpha - \beta \,\text{(twice)}$$

    - iii Calculate the delocalisation energy for the cyclopropene radical. Should we consider cyclopropene to be a delocalised molecule?

iv The E_0 to E_1 transition in cyclopropene occurs at an absorption wavelength of 200 nm. Estimate the value of the resonance integral, β, in cyclopropene.

v In reality, cyclopropene is found to be a very unstable and reactive molecule. Does this align with your Hückel calculation? If not, why not?

Extended Problems 1

1. Experimentally, it is found that when fluorobenzene undergoes electrophilic aromatic substitution:

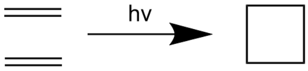
   - The reaction proceeds more slowly than it does for benzene (i.e. the fluorine is deactivating).
   - Substituents are directed towards the ortho and para positions on the ring.

   The following questions relate to these observations.

   i Set up and do a Hückel Theory calculation using HuLiS to show that Hückel theory can predict the directing effects, but actually predicts that fluorobenzene will react *faster* than benzene.

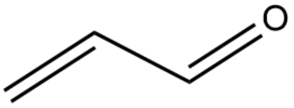
   ii Explain why Hückel Theory fails to accurately explain the kinetic observation.

2. Draw a correlation diagram to show why the [2+2] cycloaddition of ethene to ethene to form cyclobutane (below) is thermally disallowed, but allowed photochemically.



   Note: The point group of cyclobutane is D_{2d}. The conserved symmetry elements during the reaction are the σ_d mirror planes.

3. Use a Hückel Theory calculation using HuLiS to explain why α, β-unsaturated carbonyl compounds (such as acrolein, below) preferentially undergo nucleophilic attack at the terminal carbon and not the carbonyl carbon.



Lecture 6

Electron Peculiarities

Lecture Aims

- To understand the basic idea of **spin-orbit coupling**
- To understand the difference between an electron configuration and a term.
- To understand how to read a term symbol.

Today we are going to talk about electrons. We've been putting electrons into MO diagrams since we were A level students, but in reality there is more to the story than this. Different arrangements of electrons *within a given electronic configuration* can have very different energies. As we will see, this has wide application to both molecular structure and to spectroscopy.

6.1 Electron Interactions

Up until now, we've considered that the energy of a molecule is simply the sum of the energy of all the occupied MOs. This is how we used Hückel theory to rationalise all kinds of things last time. However, this is only true **within the orbital approximation** where we consider that all electrons are independent and non-interacting. How good is this approximation?

Not particularly good, obviously, because as we learnt last year a fundamental problem in trying to solve the Schrödinger equation is that electron positions are correlated. The position of one electron depends on all the others, so there must be interaction between electrons. We are going to explore this today and learn how we can label electronic states of molecules in a way that accounts for these interactions between electrons.

6.1.1 The Pauli Principle

To begin with, let's revisit something you already know about: **The Pauli Principle**. The Pauli Principle is the reason that you draw electrons in the same orbital with opposite spins, and you know that electrons in the same orbital can't have the same spin. The reason normally given for this in chemistry is: *'no two electrons can have the same set of quantum numbers'*, which is fine for most purposes[1].

We can go a bit further than this here, and give a stronger statement of the Pauli Principle. A strong statement would be:

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[1] Another way to say this is 'every occupied quantum state can only contain one electron'.

> *The total wavefunction of the system must be antisymmetric with respect to exchange of electrons.*

What this means is that **if we swap the positions of the two electrons, the sign of the wavefunction must change**:

$$\Psi(1,2) = -\Psi(2,1) \tag{6.1}$$

Equation 6.1 is a stronger statement of the Pauli Principle. If I have a system containing two electrons (1 and 2), then if I swap the positions of them, I get the negative of the original wavefunction back (this is what *antisymmetric* means in this context). This is equivalent to the 'no electrons with the same spin in the same orbital' description – if I had two electrons with exactly the same quantum numbers, interchanging their position wouldn't change anything about the wavefunction, so they'd violate Equation 6.1.

We'll use the Pauli Principle again later on. Now, let's think about interactions between electrons within a given configuration.

6.1.2 Spin-Orbit Coupling

As a motivating example, let's consider the ground state of an oxygen molecule, which we know[2] has the outer electron configuration $1\pi_g^2$. We normally draw this configuration as shown in Figure 6.1 (a), but there are other options that satisfy the Pauli Principle too (Figure 6.1 (b) and (c)). Are these different arrangements of electrons all degenerate, or do they have different energies?

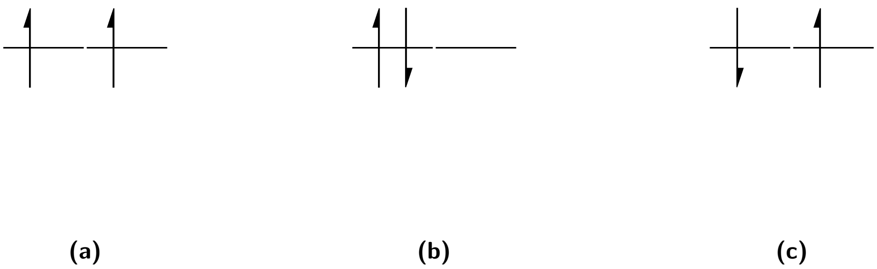
(a) **(b)** **(c)**

Figure 6.1: Possible electron arrangements of the π_g^2 configuration of O_2.

These different ways of filling the orbitals do have different energies. These are known as different **terms** that arise from the overall $1\pi_g^2$ **configuration**. These terms have different energies due to the interaction of the **spin angular momentum** and **orbital angular momentum** of the different electrons, via a process called **spin-orbit coupling**.

A good way to picture this is as the electron simultaneously *spinning* around its own axis (**spin** angular momentum) and *orbiting* around the atom/molecule it is attached to (**orbital** angular momentum). These two kinds of angular momentum *couple* together in different ways to produce states with different energies[3], and the whole process is called **spin-orbit coupling**.

Angular momentum in quantum chemistry is a *vast* topic and we aren't going to treat it much detail here[4]. The fundamental thing you need to know is that spin-orbit coupling exists, that

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[2] Look back at CH2203 for a reminder.

[3] You can think about the angular momentum vectors being added together, if that's a picture that helps.

[4] Have a look in Atkins' MQM for some further information.

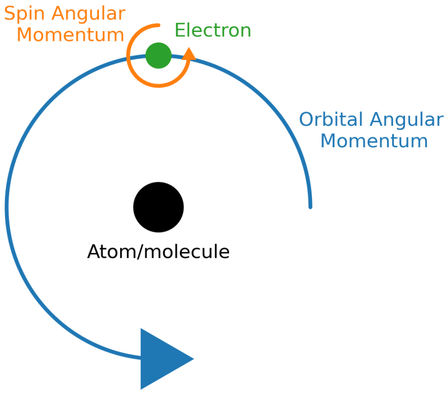

Figure 6.2: The idea of spin-orbit coupling: spin angular momentum (orange) and orbital angular momentum (blue) couple together. The orbital angular momentum defines the spatial symmetry of the wavefunction of the electron.

it comes from the interaction of spin and orbital angular momentum of electrons, and that it affects the energy of molecules. A specific combination of spin and orbital angular momenta within a given electron configuration is called a **term**.

Spin-Orbit Coupling

Spin-Orbit Coupling is a phenomenon where the **spin** and **orbital** angular momenta of electrons **couple** together to produce different **terms** from a single electron **configuration**. Different terms have different energies.

6.1.3 Term Symbols and Wavefunction Symmetry

To describe these **terms**, we use something called a **term symbol**. Term symbols are like an abbreviated way to explain the arrangement of electrons in a molecule (and therefore the spin-orbit coupling) without having to draw the full MO diagram. A variety of term symbols for atoms and molecules are given below:

$$^1D_0,^3\Pi_u,^2P_1,^1\Sigma_g^+,^1A_1,^3B_2$$

You can see that they all have a lot of subscripts and superscripts. Different species have different notation here but there are some commonalities. The first superscript and the large letter correspond to:

$$^{\text{Spin Multiplicity}}(\text{Spatial Symmetry})$$

To understand this, we need to understand that fundamentally, **the term symbol is describing the symmetry of the electronic wavefunction of the atom/molecule**, which is what changes when you shuffle around electron spins and put things in different orbitals. The total electronic wavefunction can be expressed as a product of a spatial and a spin wavefunction:

$$\Psi_{\text{Total}} = \psi_{\text{space}} \times \psi_{\text{spin}} \tag{6.2}$$

The spatial and spin wavefunctions relate to the orbital and spin angular momenta respectively[5]. So the term symbols specify the arrangement of spin and orbital angular momenta, and by extension the symmetry of the spin and spatial parts of the electronic wavefunction under the symmetry elements of the atom/molecule. Let's now look at how we can interpret and understand the various bits of a term symbol, building up to understanding the whole thing.

Disclaimer: *Term symbols are notoriously annoying to understand when you're a student (or, they were for me 10 years ago). Most of this is because actually understanding how all the angular momentum coupling results in different terms requires a lot more maths than we have time to do in this course. Here, we will be focussed on two things:*

1. *Understanding what the term symbol physically represents.*
2. *Understanding how to use term symbols to rationalise chemistry.*

Neither of these aims really requires that we know how to do angular momentum algebra ourselves in any detail, so we won't do that here. I've tried to find a new way to explain it that doesn't require all the algebra...

Spin Multiplicity

The spin multiplicity is probably the easiest part of a term symbol to understand. It tells you the possible arrangements of the spin angular momenta of the electrons in the outer shell of the atom or molecule. The spin multiplicity is given by $2S + 1$§ where S is the total spin angular momentum quantum number. The spin multiplicity takes integer values that correspond to the number of unpaired electrons in the system:

- $\boldsymbol{2S+1=1} \rightarrow S = 0 \rightarrow$ **singlet** state (no unpaired electrons).
- $\boldsymbol{2S+1=2} \rightarrow S = \frac{1}{2} \rightarrow$ **doublet** state (one unpaired electron).
- $\boldsymbol{2S+1=3} \rightarrow S = 1 \rightarrow$ **triplet** state (two unpaired electrons).
- $\boldsymbol{2S+1=4} \rightarrow S = \frac{3}{2} \rightarrow$ **quartet** state (three unpaired electrons).
- ... and so on.

Hopefully this is at least a bit familiar, given that we know individual electrons have a spin of $^1/_2$. For example, in the oxygen MO diagrams in Figure 6.1, we have spin multiplicities of 3, 1, and 1 for panels (a), (b), and (c). So our oxygen molecule in the ground state *configuration* produces three *terms*: a triplet term, and two singlet terms. We'll see what to do with this information shortly.

Spatial Symmetry

The spatial symmetry is slightly more fiddly to understand. In general, **the spatial symmetry of the electronic wavefunction is defined by it's symmetry representation in the point group of the molecule**. For example, if we were looking at the spatial symmetry of the electronic wavefunctions of water (C_{2v} point group), they might have A_1, A_2, B_1 or B_2 symmetry.

In simple cases like atoms and diatomic molecules we can work out the spatial symmetry from the electron configuration using angular momentum coupling algebra. We won't do this explicitly

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[5] Think of the orbital angular momentum as defining the shape of the wavefunction as the electron orbits around the nucleus - the path of the orbit defines the shape.

here, but in the case of atoms and diatomics it's relatively easy to relate the spatial symmetry of the wavefunction to the orbital angular momentum of the electrons. Remember that the angular momentum quantum number is L for atoms (or Λ for diatomic molecules):

- $\boldsymbol{L = 0} \rightarrow$ S term (Σ for diatomics).
- $\boldsymbol{L = 1} \rightarrow$ P term (Π for diatomics).
- $\boldsymbol{L = 2} \rightarrow$ D term (Δ for diatomics).
- $\boldsymbol{L = 3} \rightarrow$ F term (Φ for diatomics).
- ... and so on.

Hopefully you can see that this nomenclature just mirrors the familiar 's, p, d, f' nomenclature for atomic orbitals – these labels are just symmetry labels, after all. Now we will see how we derive possible term symbols from an electron configuration.

To use the example of the oxygen molecule again, we first find the point group of the molecule ($D_{\infty h}$). Then we look at the group theory table and notice that there are absolutely loads of possible symmetries of the electronic wavefunction, ~~get demoralised, jack it all in, and go to the pub~~ *and realise we need an easy method to go from the electronic configuration (π_g^2) to the term symbols.*

6.1.4 Direct Products

Symmetry will come to the rescue again here. First of all, let us say for now that we can neglect all electrons except the partially-filled valence shell (we will justify this shortly). Then, we notice that our valence shell contains two electrons (π_g^2), and we already know the spatial symmetry[6] of the orbitals each of those electrons is in is π_g. The symmetry of the *overall* wavefunction will then just be given by the **direct product** of the symmetries of the two individual electrons:

$$\pi_g \otimes \pi_g = \Sigma_g^+ + [\Sigma_g^-] + \Delta_g \tag{6.3}$$

Where the $\otimes$ symbol means **direct product**, and we got the answer to the product by looking in the **direct product tables** at the back of our group theory booklet. You can think of a direct product as just like the group theory equivalent of multiplication[7]. In this case, we get the table for the $D_{\infty h}$ point group, and we work out the g and u labels from another direct product table in the booklet. I'll show you how it works in the lecture.

This tells us that the spatial wavefunctions we get from the π_g^2 configuration have Σ_g^+, Σ_g^-, and Δ_g spatial symmetry. These are all irreps of the $D_{\infty h}$ point group. The only thing left to do to find the complete term symbols is to work out what spin multiplicity is in each case. Helpfully, Equation 6.3 tells us this too – the square brackets around the Σ_g^- term basically mean that this term has a spin wavefunction with triplet multiplicity, and the absence of square brackets mean that the other two have singlet multiplicity[8]. Thus, overall, we have the following term symbols for the π_g^2 configuration:

$$^1\Sigma_g^+, {}^3\Sigma_g^-, {}^1\Delta_g$$

That was exciting. There are a couple of quick technical points to make before we move on:

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[6] All those σ and π bonds, s, p, and d orbitals etc.. are just labels describing the symmetry of electronic wavefunctions. Just you may not have realised it before :)

[7] Actually, the direct product is a matrix multplication, because these symmetry irreps are really matrices that represent the symmetry of an object within a point group. Again, matrices are everywhere.

[8] Alright - this is a simplification. Really the square brackets mean that the spatial wavefunction is *antisymmetric*, so to satisfy the Pauli Principle it needs to be paired with a *symmetric* spin wavefunction. Triplet spin wavefunctions are symmetric, hence the term symbols given.

- We only care about the outermost, unpaired electrons. This is because any closed shell configuration will transform as the **totally symmetric irreducible representation (TSIR)** of the point group (the one that has $+1$ for all it's characters, at the top of the character table). The direct product of any irrep with the TSIR will not change the orignial irrep.
- If we have just one electron, then we obviously don't need to do direct products. The symmetry of that one electron will tell us the symmetry of the overall wavefunction.
- If we have more than two electrons, we can do multiple direct products in turn[9]. However, it's often easier to rework the system into something where you have just two things to take a direct product between (we will see this later).
- Notice that our individual electrons on atoms had lower case (π) labels, but that the overall molecule has an upper case (Π) label. This is a general convention: upper case for molecules, lower case for the constituent atoms.

Let's calculate some other term symbols with different numbers of electrons to practice the process, and then move on to seeing how this is in any way useful.

Term Symbols

Using direct product tables where necessary, calculate term symbols for the following electron configurations:

- σ_g^2 in the $D_{\infty h}$ point group (e.g. H_2).
- π_u^1 in the $C_{\infty v}$ point group (e.g. HC radical)
- b_1^2 in the C_{2v} point group (e.g. water)

6.1.5 Hund's Rules

Having found our three terms arising from the π_g^2 configuration, the natural question is to ask what the energy ordering of those terms is. The energy ordering is basically dictated by to what extent the electrons repel each other in a given term: more repulsion $=$ higher energy.

In simple cases (atoms and diatomics) we can work out the energy ordering using **Hund's Rules**. They only really apply for ground state configurations of atoms, but work well enough for bigger systems in some cases. Hund's rules state:

1. The term with the highest spin multiplicity is the lowest energy (so triplets are lower energy than doublets or singlets).
2. For terms with the same spin multiplicity, the term with the most orbital angular momentum is the lowest energy (so a Δ term is lower energy than than a Σ term of the same multiplicity)[10].

There is a third rule that only applies to atoms. Hund's first rule (about spin) applies very widely. The second rule applies less widely and only really to diatomics in the cases we are going to look at. **In general, there's not an easy and obvious to find out the energy ordering of electronic states just from their symmetry labels** – but you can sometimes use the symmetry to help you make good guesses, which we will see next time.

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[9] But doing this can give a result that isn't trivial to interpret, because you end up with states that have spatial symmetry that is neither symmetric or antisymmetric...

[10] Remind me to explain this mid-lecture.

Fermi Holes

To understand the spin multiplicity rule, we have to think about wavefunction symmetry again. If the spin wavefunction is symmetric with respect to exchange of the electrons (as in a triplet state)[11], then the spatial wavefunction of the electrons has to be antisymmetric via the Pauli principle. Mathematically, this means:

$$\Psi_{space}(1,2) = -\Psi_{space}(2,1) \tag{6.4}$$

i.e. if we swap the positions of the electrons, we flip the sign of the wavefunction. If we now imagine the limit where the two electrons are in the same place, then position 1 is the same as position 2, so (with only a slight abuse of notation) we have:

$$\Psi_{space}(1,1) = -\Psi_{space}(1,1) \tag{6.5}$$

The only way this can be true is if

$$\Psi_{space}(1,1) = 0 \tag{6.6}$$

So, for an asymmetric spatial wavefunction, the wavefunction has to be zero when the electrons are in the same position. Yet, obviously, if the wavefunction is zero there is no chance that the electrons can be in this position. **The upshot is that with a asymmetric spatial wavefunction, the electrons cannot approach each other because the wavefunction vanishes as they do**. This reduces electron-electron repulsions, and is called a **Fermi hole**. The reduced repulsion lowers the energy of this spatial wavefunction. These asymmetric spatial wavefunctions have to always be paired with symmetric spin wavefunctions (via the Pauli principle), and the result is that terms with symmetric spin wavefunctions (triplets) are lower energy than those with antisymmetric spin wavefunctions (singlets).

You can make an analogous argument to show that the wavefunction of a symmetric spatial wavefunction approaches a maximum as the electrons approach each other - raising the energy. **The first person to prove this will win an undisclosed prize.**

6.2 Applications of Term Symbols and MO Diagrams

Now we can look at some places where term symbols prove incredibly useful in chemistry – places where spin-orbit interaction really matters. We will see a couple of examples here.

6.2.1 Electronic Spectroscopy

In electronic spectroscopy, we are using light to drive transitions between electronic states of a molecule. That means that the transitions happen between different terms[12].

We can illustrate this using our low-lying states of O_2 again. To know if we can have transitions between these states, we need to know the **selection rules** that govern the transitions. In general for electronic spectroscopy, there is one key selection rule (see the Spectroscopy part of this module for more detail):

$$\Delta S = 0$$

The light cannot change the spin of the electronic state. This rule applies relatively widely, but as you know from last year there are places where it gets relaxed (like in d-d transitions of metal complexes). So can we use light to drive a transition from our ground state of O_2 to any excited states?

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[11] Imagine swapping the positions of the two electrons in Figure 6.1 panel (a) – the configuration is the same.

[12] And between different levels and states within those terms, sometimes – a story for another time

We can't, because either of the transitions:

$$^3\Sigma_g^- \rightarrow ^1\Delta_g \; ^3\Sigma_g^- \rightarrow ^1\Sigma_g^+$$

Break the spin selection rule. As evidence of this, if you excite molecular oxygen you find that the excited state lives for a very long time – over an hour. This is because the only way it can de-excite is via a spin-forbidden process, so it is very slow. Next time we will talk about how we can also use the **transition dipole moment** to rationalise this behaviour.

6.2.2 Rationalising Structure and Reactivity

Let's look at the oxygen terms to rationalise some chemistry. Experimentally, it is found that:

- The ground state of molecular oxygen is paramagnetic (attracted to a magnetic field)
- Two low-lying excited states of molecular oxygen are diamagnetic (unaffected by a magnetic field).
- The bond length and O-O vibrational frequency of molecular oxygen in all the aforementioned states are very similar to one another.

We can explain all of these observations using our MO diagrams and the corresponding term symbols.

Para- and Diamagnetism

The first two observations are relatively simple to explain. A molecule will be **paramagnetic**, and attracted to an external magnetic field, if it has unpaired electrons[13]. If it does not have any unpaired electrons, it will be **diamagnetic**, and unaffected by the field.

Looking at an oxygen MO diagram for our three possible terms (Figure 6.1), clearly only the $^3\Sigma_g^-$ state has unpaired electrons. We know that this is the ground state via Hund's rules, so that explains our first observation. The next two excited states are both singlet states (no unpaired electrons), so will be diamagnetic – explaining our second observation.

Bond Lengths and Vibrations

It's observed that all three low-lying electronic states of O_2 have very similar bond lengths and vibrational frequencies – even though they have quite different energies.

The reason for this is that to make these excited states, *we didn't move an electron out of the* π_g *orbital into another orbital.* Because the molecular structure and bond strength/stiffness is mostly determined by the orbitals the electrons are in (and not the specific arrangement of the electrons within these orbitals), the three low-lying states of O_2 all have very similar bond length and vibrational frequencies. They do have different energies, however – and we will see the impact this has in one of the problems.

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[13] This is because of the magnetic moment of an unpaired electron, which is lost when the electrons pair up (the two magnetic moments cancel out).

Take Home Messages

- The energy of a molecule is not simply given by the sum of the energies of the occupied orbitals, but depends on the specific arrangement of electrons.
- The specific arrangement of electrons matters due to *spin-orbit coupling*.
- We use **term symbols** to describe the different electronic states of molecules that arise from spin-orbit coupling.

Lecture 7

Bigger Molecules: Symmetry

Lecture Aims

- To understand how to use symmetry and group theory to determine symmetries of orbitals in larger molecules.
- To use the symmetry and group theory to construct MO diagrams.
- To start to understand what a *symmetry adapted linear combination* of AOs is.

Today, in our last lecture, we are going to see how we can use group theory to work out the symmetries of MOs in larger molecules – and explain some interesting chemistry along the way.

We haven't spoken about symmetry much in this course, but we've also been focussed on examples like diatomics (which are straightforward), and on conjugated polyenes that we can treat using Hückel Theory (and thus bypass a lot of the complexity). Today let's see how we can build up MOs of larger molecules from more than two AOs using group theory.

7.1 AO Symmetry

Firstly let's reiterate the most important thing symmetry does for us in this context:

- AOs can only mix with other AOs **of the same symmetry**.
- Thus, if we can find the symmetry of all the AOs in a molecule, we should be able to find the symmetry of the MOs, and thus start rationalising the chemistry of the molecule.

So, how do we find the symmetry of AOs in a given molecule? We need to construct **symmetry representations** of the AOs in the point group of the molecule, using the character tables that we used last year in CH2200.

7.1.1 A Simple Example: H_2

Let's illustrate this for a simple molecule like H_2 to start, and check that we get the same result we expect from previous MO theory (two MOs with σ symmetry). The steps are as follows:

1. Determine the AOs that are contributing to the bonding.
2. Determine the symmetry representation of these AOs in the point group of the molecule.

3. Determine how these AOs will combine with each other to produce MOs.

For H_2, clearly the two AOs that contribute to the bonding are the 1s orbitals on each H atom. The point group of H_2 is $D_{\infty h}$, so what is the symmetry of this **pair** of 1s orbitals in the $D_{\infty h}$ point group? We work this out by finding the character of the of this pair of orbitals under each operation in the point group, just as we did in CH2200: Remember that:

$D_{\infty h}$	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C_2'$
$\Gamma(H1s)$	2	2	...	2	0	0	...	0

- If an orbital is unchanged under the operation, it contributes +1 to the character.
- If an orbital is moved to a different location under the operation, it contributes 0 to the character.
- If the orbital is mapped onto a reversed version of itself under the operation, it contributes -1 to the character.

We then need to reduce this representation to a sum of irreducible representations (irreps). We can see by inspection that $\Gamma(H1s)$ in the table above will reduce to:

$$\Gamma(H1s) = \Sigma_g^+ + \Sigma_u^+$$

These are the symmetries of the H 1s orbitals in the point group of H_2, and **thus are also the symmetries of the resultant MOs**. This is entirely in line with what we expect, right? Two MOs with σ_u and σ_g symmetry (note that the convention is to use lower case letters to refer to the orbitals, and upper case to refer to the actual irrep).

7.1.2 Water

Now let's try a more complex example: water. Water is in the C_{2v} point group, and the orbitals involved in the bonding are the 1s orbitals on the hydrogens, and the 2s and 2p orbitals on the oxygen. What are the symmetries of these orbitals?

Ligand Group Orbitals

In a molecule like water, we clearly have a central atom (oxygen) and then a set of 'ligands' that are bound to it (the hydrogens). In doing this kind of MO analysis, we normally group the ligand orbitals all together as a set, rather than thinking of them individually. So we find the symmetry representation of the whole set, sometimes called a **ligand group orbital** (LGO). For water, the two H 1s orbitals from a LGO with symmetry representation: Which reduces by inspection to

C_{2v}	E	C_2	σ_v	σ_v'
$\Gamma(H1s)$	2	0	0	2

$A_1 + B_2$. So our H 1s orbitals span the $A_1 + B_2$ irreps. We can see relatively intuitively that these must correspond to the in-phase and out-of-phase combination of the two 1s orbitals, as in Figure 7.1. These combinations of the AOs into combinations that have symmetry in a given point group are called **symmetry adapted linear combinations**, or **SALCs**. You can construct SALCs in general using a method called the **projection operator** method, which you'll learn about later in the course – for the examples we'll see here, we can use logic and intuition to work out what they must look like.

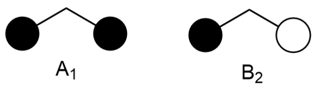

Figure 7.1: The H 1s orbitals combine in the C_{2v} point group to give two SALCs with A_1 and B_2 symmetry.

Central Atom Orbitals

Now we have the symmetry representation of the H 1s orbitals, we can turn to the 2s and 2p orbitals on the oxygen. We can read the symmetry of these orbitals straight from the C_{2v} character table:

- The 2s orbital must be totally symmetric (spherical[1]), so has A_1 symmetry.
- The 2p orbitals have the same symmetry as the coordinate axes:
  - $2p_z \rightarrow A_1$ symmetry.
  - $2p_x \rightarrow B_1$ symmetry.
  - $2p_y \rightarrow B_2$ symmetry.

Now we know the symmetry of all the AOs in water, let's see how they combine to produce the MOs on an MO diagram (Figure 7.2). Remember that orbitals can only mix with orbitals of the same symmetry.

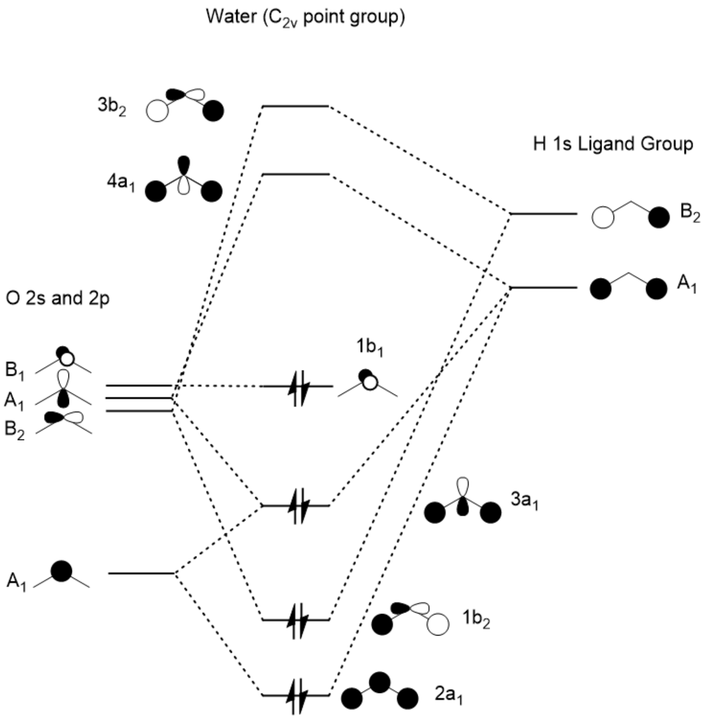

Figure 7.2: MO diagram of water. Orbital symmetries are sketched and denoted with their irrep in the C_{2v} point group. Note that the 2p orbitals on the oxygen are degenerate, but shown separated for clarity.

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[1] Same symmetry as $x^2 + y^2 + z^2$ – the equation for a sphere.

Now, we drew this diagram, but actually the symmetry alone isn't enough information to draw out this, as the symmetry doesn't tell you anything about the energy ordering. We can rationalise this to some extent though:

- The 2s orbital (A_1) will be at lower energy than the 2p orbitals ($A_1 + B_1 + B_2$).
- The H 1s orbitals will be of a slightly higher energy to the O 2p orbitals, due to the decreased nuclear charge in H.
- The $1b_1$ MO will be non-bonding, because there are no ligand orbitals with B_1 symmetry.
- The ligand AO with A_1 symmetry will be lower in energy than the one with B_2 symmetry (see above).
- Orbitals that are closer together in energy will mix more strongly.

But really, to accurately know the energy ordering of the MOs requires proper quantum chemical calculations. We can get a feel for what the MOs look like, though - this is drawn on Figure 7.2 for each MO.

Chemistry?

What does the MO diagram of water we just constructed tell us about chemistry? Well, there are a few things:

- Water doesn't *really* have two non-bonding lone pairs, unlike what VSEPR theory tells us. Only one lone pair is truly non-bonding (in the $1b_2$ orbital).
- There are three orbitals with bonding character ($2a_1, 1b_1, 3a_1$).
- The HOMO of water is the lone pair on the oxygen – so this is where water will react as a nucleophile, as we'd expect.

You can repeat this process for other small molecules (see problems about ammonia and methane).

7.2 Metal-Ligand Complexes

We said at the start of this course that we'd work our way up to using quantum mechanics to understand some parts of organic and inorganic chemistry. We've done the organic part with Hückel Theory, and now we can use our new knowledge of symmetry and group theory to understand some inorganic chemistry too.

We're going to look at the MOs of **metal-ligand complexes**. Things with a general formula like ML_6 or ML_4. We'll see that we can use our group theory to explain lots of chemistry about these kinds of complexes.

7.2.1 Octahedral and Tetrahedral Splitting

The first thing we'll do is think about the symmetry of the orbitals on the metal centre. If we restrict ourselves to thinking about the first row of the d-block, the valence orbitals will be the 3d, 4s, and 4p orbitals. So we need to know the symmetry representation of these orbitals in the point groups of the overall metal complex.

We can work this out, because the character tables will helpfully tell us how the different orbitals transform:

- s orbitals always transform as the totally symmetric irrep (top row).
- p orbitals transform with the same symmetry as the linear x, y, and z functions.
- d orbitals transform with the same symmetry as the quadratic $xy, yz, xy, x^2 - y^2$, and $2z^2 - x^2 - y^2$ functions.

So, if we took an octahedral complex (O_h) point group:

- The 4s orbital has A_{1g} symmetry.
- The 4p orbitals have T_{1u} symmetry.
- The 3d orbitals have E_g and T_{2g} symmetry.

Can you see now why people label set of d-orbitals with e_g and t_{2g} symmetry labels? Remember that we use *upper case* when referring to the original irrep, and *lower case* when referring to the MO.

There is another point worth making here about irreps, which is that those that begin with E represent **doubly degenerate** irreps, and those that begin with T represent **triply degenerate** irreps. So, we have *two* d-orbitals with equal energy of e_g symmetry , and *three* degenerate d-orbitals with equal energy of t_{2g} symmetry on our metal ion in an octahedral ligand field.

Tetrahedral d-orbitals

What are the symmetries of the metal d-orbitals in a tetrahedral complex (T_d symmetry)?

7.2.2 Ligand Symmetries

We will restrict ourselves to thinking about the ligands around our complex as simple electron pair donors, donating electrons though a σ bonding interaction[2]. Remembering that we have to treat the ligands as a group, we can work out the symmetry representation of these six ligands as:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma(L_6)$	6	0	0	2	2	0	0	0	4	2

Which reduces to $E_g + T_{1u} + A_{1g}$. So our six ligand orbitals in an octahedral field become an orbital with a_{1g} symmetry, two degenerate orbitals with e_g symmetry, and three degenerate orbitals with t_{1u} symmetry. We won't worry about the exact combination of our original AOs that forms each of these SALCs here[3].

Tetrahedral ligand orbitals

What are the symmetries of the four ligand orbitals in a tetrahedral complex (T_d symmetry)?

With this, and the symmetry of the metal orbitals, we can draw out the MO diagram of an octahedral ML_6 complex.

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[2] We can then think of the ligands as just s-orbitals, for the purposes of making this representation – or p orbitals pointing along the axes of the complex if you want to be more precise.

[3] See, for example, *Inorganic Chemistry*, by Weller, Overton, Rourke, and Armstrong – section 20.2.

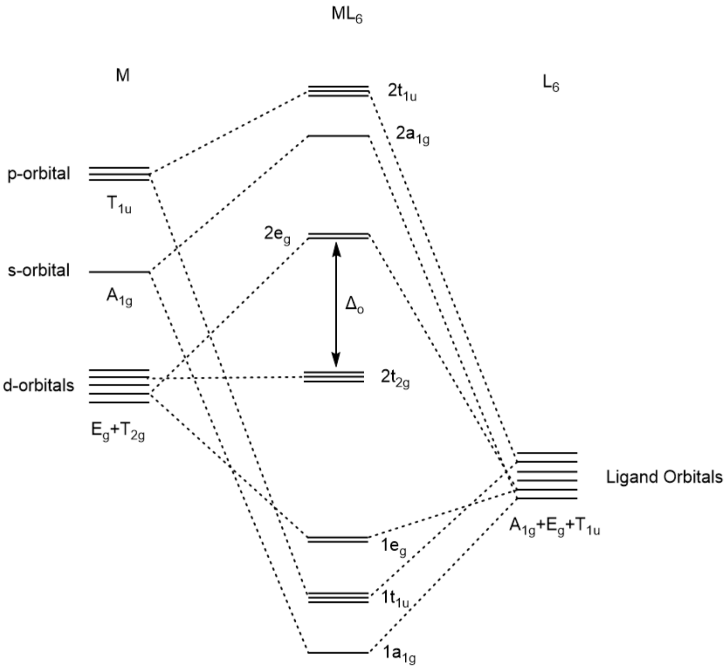

Figure 7.3: Unfilled MO diagram of an octahedral ML_6 complex where the ligands donate through σ interactions. Note closely spaced orbitals are degenerate. The octahedral splitting parameter, Δ_o is annotated.

Note, again, that the exact energy ordering can't be calculated directly from the symmetry, but we can make an educated guess as to what it will be.

7.2.3 Chemistry?

We can rationalise some chemistry using this picture. Firstly, we can see that the bonding orbitals **mostly have ligand character** – which should make some sense, as the ligands are more electronegative and supply the electrons that form the bonds. The anti-bonding orbitals **mostly have metal character**, in contrast.

Splitting Parameters

Secondly, illustrated on Figure 7.3 is the **octahedral splitting parameter**, Δ_o. This is defined as the gap between the non-bonding t_{2g} orbital and the higher lying e_g orbital. This is relevant because if each ligand provides two electrons, then the metal d-electrons are the ones that fill the t_{2g} and the e_g – these are our frontier orbitals, and the ones that govern reactivity.

The splitting parameter just depends on the energies of the ligand orbitals relative to the metal. Because the t_{2g} orbital is non-bonding, only the e_g will vary in energy as the ligand energies change – if the ligand energies get *closer* to the energies of the metal orbital, then Δ_o will increase, and vice versa. This has it's most obvious implication in spectroscopy, where ligands are ranked by the energy of the $e_g \rightarrow t_{2g}$ transition, in the **spectrochemical series**.

High and Low Spin

The splitting parameter also has a direct influence on the chemistry, because (amongst other things) it affects whether or not the complex is **high spin** (with as many electrons unpaired as possible) or **low spin** (with electrons paired up). I'll draw this out for you in the lecture if you need a recap - but you can imagine the difference between two d^5 configurations: the *low spin* configuration would have $t_{2g}^5 e_g^0$ with only one unpaired electron. The *high spin* configuration would have $t_{2g}^3 e_g^2$ with five unpaired electrons.

To rationalise this, we know that electron-electron repulsions are destabilising, and so electrons would rather be unpaired if they could be. However, this destabilisation due to spin has to be balanced with the destabilisation that occurs when a higher energy orbital (the e_g) is filled. A ligand that increases Δ_o raises the energy of the e_g orbital and is thus more likely to form low-spin complexes, because the energy cost of promoting an electron to the higher energy e_g orbital outweighs the penalty associated with spin-pairing. It's all just about minimising energy.

7.3 A Final Look at Spectroscopy

Finally, we're going to take a first look at how we can use symmetry to help us predict spectra. We briefly mentioned this in CH2200, and it will be mentioned again later in this course.

7.3.1 Transition Dipole Moments

The fundamental idea is that the intensity of any electric dipole transition (i.e. one stimulated by absorption or emission of light) between an initial state Ψ_i and a final state Ψ_f is proportional to the square of the **transition dipole moment (TDM)** between those two states. The TDM is an integral given by:

$$\text{TDM} = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle \tag{7.1}$$

Here $\hat{\mu}$ is the **dipole moment operator**, which is the operator that couples together to the two states Ψ_i and Ψ_f. To understand what this means, note that $\hat{\mu}$ operates on Ψ_i first, to give a new state. Let's call this new state Ψ_i':

$$|\Psi_i'\rangle = \hat{\mu}\,|\Psi_i\rangle$$

This new state is like the state you get once the photon hits the initial state and excites it. The overall 'success' of the transition depends on the overlap between this new state and the actual final state:

$$\langle \Psi_f | \Psi_i' \rangle = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle = \text{TDM}$$

The TDM is what ultimately gives rise to all of the selection rules that exist in spectroscopy. You'll hear more about this in the next part of the course.

For now, let's just focus on one important thing. Clearly, if the TDM is zero, then we have no transition intensity, and so no transition. Thus, if we can find out whether or not the TDM is non-zero, that will at least give us some information about which transitions are possible to see in our spectra. The TDM is just an integral, so, how do we determine if an integral is zero or non-zero?

7.3.2 Integral Symmetry and Direct Products

Symmetry comes to the rescue again. Recall that an integral of an odd function over all space is always zero - if we can show that our TDM integrand either is or isn't an odd function, then we will know whether or not the corresponding transition has non-zero or zero intensity. We can do this by simply taking the direct product of the symmetries of the three terms inside the TDM:

$$\Gamma(\Psi_f) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\Psi_i) \tag{7.2}$$

If this product **contains the totally symmetric irreducible representation**, then the integrand isn't an odd function and the integral is non-zero. Conversely, if the product in Equation 7.2 doesn't contain the TSIR, then the integral is zero. So by doing this direct product we will be able to work out which transitions are going to appear, or not appear in our spectrum[4]. So what are the symmetries of the three things in the TDM?

We know the symmetries of the initial and final states from MO diagrams, or we are given them, or we work them out. The dipole moment operator $\hat{\mu}$ has three components $(\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z)$ with the same symmetry as the coordinate axes. As an example, let's see if a transition between a singly occupied b_1 HOMO (initial state) and a_1 LUMO (final state) is allowed in water. We consider each axis of the dipole operator (remembering the convention of lower case for the orbital, upper case for the irrep):

- Along $x \rightarrow B_1 \otimes B_1 \otimes A_1 = A_1 \otimes A_1 = A_1 \rightarrow$ **allowed**.
- Along $y \rightarrow B_1 \otimes B_2 \otimes A_1 = A_1 \otimes A_1 = A_2 \rightarrow$ **disallowed**.
- Along $x \rightarrow B_1 \otimes A_1 \otimes A_1 = A_1 \otimes A_1 = B_1 \rightarrow$ **disallowed**.

Remember that the transition is only allowed if the product contains the TSIR (A_1 in the C_{2v} point group. Hence, the $b_1 \rightarrow a_1$ transition is electric dipole allowed, with transition dipole moment along x. Note that usually we would have to work out the term symbol corresponding to a complete electronic configuration before we do this – but this is a topic for later. The direction of the TDM is useful in more advanced kinds of spectroscopy, come and ask if you want to know more. You'll see this again in much more detail in the next part of the course, so don't panic if this quick introduction felt rushed!

Anyway, that's it from me. Now you need to **do the problems**, which is the only way to learn this material properly. We'll have a couple more sessions to go through some problems after this lecture. I hope you enjoy the next parts of the course, on spectroscopy (with more group theory), and statistical mechanics (a beautiful subject, and with far less group theory).

Take Home Messages

- The energy of a molecule is not simply given by the sum of the energies of the occupied orbitals, but depends on the specific arrangement of electrons.
- The specific arrangement of electrons matters due to *spin-orbit coupling*.
- We use **term symbols** to describe the different electronic states of molecules that arise from spin-orbit coupling.

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[4] Again, note that the symmetry doesn't actually tell you anything about transition intensity - we would need to do a numerical calculation of the TDM to find that out, which is harder.

Problem Sheet 3

1. Briefly explain the meaning of the following terms/concepts:
    - i *The Pauli Principle*
    - ii *Spin-Orbit Coupling*
    - iii *Term Symbol*
2. A reactive form of oxygen is *singlet oxygen*, which is O_2 in the $^1\Delta_g$ state, a state which lies 0.97 eV above the ground state. Singlet oxygen can decay to the ground state via a *radiative* process (emitting a photon). Calculate the wavelength of the emitted light, and qualitatively estimate the rate of this decay process.
3. Account for the following observations:
    - i The term symbol for the ground state of O_2 is $^3\Sigma_g^-$.
    - ii The term symbol for the ground state of C_2 is $^1\Sigma_g^+$.
    - iii The bond length of $O_2{}^+$ is shorter than neutral O_2, but the bond length of $N_2{}^+$ is longer than neutral N_2.
4. This question is about ammonia, NH_3.
    - i What is the point group of ammonia?
    - ii Find the symmetry representation(s) of the nitrogen 2s and 2p orbitals on ammonia within this point group.
    - iii Find the symmetry representation(s) of the three hydrogen 1s orbitals *as a ligand group* on ammonia within this point group.
    - iv Hence sketch an MO diagram of ammonia, identifying the HOMO and LUMO.
    - v Use your MO diagram to explain why the electrons on ammonia are mostly found near the central nitrogen atom.
5.
    - i Heme is a molecule in the D_{4h} point group that contains iron. Heme is found in many proteins and enzymes, and has a ground state with $^1A_{1g}$ symmetry, and two excited states each with ^1E_u symmetry. Determine if transitions between the ground state and these excited states are electric-dipole allowed.
    - ii Using the transition dipole moment, explain why the d-d $t_{2g} \rightarrow e_g$ transitions are disallowed in octahedral complexes.

Extended Problems 2

1. Methane (CH_4) is a tetrahedral molecule.
    a) By doing the appropriate group theory, draw an MO diagram for methane.
    b) What is the term symbol for the electronic ground state of methane?
    c) An alternative approach to rationalising the bonding in methane is to use four equivalent sp^3 *hybrid orbitals* to hold the electrons. Photoelectron spectroscopy of methane (which probes the occupied MOs) shows two bands, with a 1:3 intensity ratio.

        Explain which picture of the bonding in methane (either hybrid orbitals, or your constructed MO diagram) is most consistent with the spectroscopic data, and hence which is more correct[5].
2. Construct an MO diagram for:
    i Water, in it's normal geometry (check lecture notes...).
    ii Water, if it was linear ($D_{\infty h}$).

    Hence explain why water is not a linear molecule.
3. Explain what is meant by the *Jahn-Teller Effect*[6]. Using the character tables for the O_h and D_{4h} point groups, determine how the symmetry of the metal d-orbitals change under a Jahn-Teller distortion, sketching a diagram to explain your reasoning.

    Which d-electron configurations would you expect to undergo Jahn-Teller distortions?

---

[5] Organic chemists hate me.

[6] Think back to inorganic chemistry modules!

Appendix A

Expectation Values

The expectation value expression makes more sense when you remember that the basis set you're expanding in is normally chosen to be a collection of eigenfunctions of the operator you're evaluating. For example, if we take the energy expectation value as an example:

$$\langle E \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

We can expand Ψ in a basis set:

$$\Psi = \sum_i c_i \phi_i$$

If these basis set wavefunctions are eigenfunctions of the Hamiltonian, $\hat{H}$ (i.e. they solve the SE), then:

$$\hat{H} \left| \phi_i \right\rangle = \epsilon_i \left| \phi_i \right\rangle$$

Where ϵ_i is the energy of ϕ_i, and:

$$\begin{aligned} \langle c_i \phi_i | \, \hat{H} \, | c_i \phi_i \rangle &= c_i^2 \epsilon_i \langle \phi_i | \phi_i \rangle \\ &= c_i^2 \epsilon_i \text{ if } \phi_i \text{ is normalised} \end{aligned}$$

So we can write our overall expectation value:

$$\begin{aligned} \langle E \rangle &= \frac{\langle \sum_i c_i \phi_i | \hat{H} | \sum_i c_i \phi_i \rangle}{\langle \sum_i c_i \phi_i | \sum_i c_i \phi_i \rangle} \\ &= \frac{\sum_i c_i^2 \epsilon_i}{\sum_i c_i^2} \end{aligned}$$

I've only summed over one variable for simplicity, and because we assume that ϕ_i are **orthonormal** (orthogonal and normalised) basis functions - so $\langle \phi_i | \phi_j \rangle = 0$ if i and j are different. This is reasonable as we can always either choose basis functions that will be orthonormal, or make basis functions orthonormal via scaling and something called the *Gram-Schmidt Process*. Now we can see that:

$$\langle E \rangle = \frac{\sum_i c_i^2 \epsilon_i}{\sum_i c_i^2}$$

So what does this mean? Well, remember the Born interpretation and the idea that the expansion coefficients within a basis set correspond to a probability amplitude – so the square of the expansion coefficient is a probability, $c_i^2 = p_i$. So:

$$\langle E \rangle = \frac{\sum_i p_i \epsilon_i}{\sum_i p_i}$$

In some ways it's clearer now to drop the sum notation:

$$\langle E\rangle = \frac{p_1\epsilon_1 + p_2\epsilon_2 + p_3\epsilon_3 + \ldots}{p_1 + p_2 + p_3 + \ldots}$$

So the numerator is a sum of the energies of each basis function, weighted by their probability of occurring. The denominator is just the sum of all the probabilities, which we can call p_{total}. $p_{\text{total}} = 1$ if we started with a normalised wavefunction Ψ. Thus, for a normalised wavefunction and orthonormal basis functions:

$$\langle E\rangle = p_1\epsilon_1 + p_2\epsilon_2 + p_3\epsilon_3 + \ldots = \sum_i p_i\epsilon_i$$

Which is just the definition of a mean value (*'add up all the numbers and divide by the number of numbers'* is the same thing as *'add up all the numbers multiplied by their probability of occurring'*). So you can see that the expectation value of an observable (here the energy) is basically just the average value that the observable takes in a given basis set. *'Add up all the possible energies of the system, weighted by their probability of occurring'*.

Appendix B

Proof of The Variational Theorem

Alright. I'm going to do this in the most elegant way I know, which is the way I was taught as an undergraduate by David Manolopoulos[1]. There are other ways which are perhaps clearer, but are clunkier and much less elegant. This is an appendix and not something you need to worry about for the exam, so elegance takes precedence over absolute clarity.

We start with the familiar expectation value:

$$\langle E \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

We now assume that we can expand $|\Psi\rangle$ in an orthonormal basis: $|\Psi\rangle = \sum_i c_i |\phi_i\rangle$. This basis is composed of eigenfunctions of the Hamiltonian, $\hat{H}$, (i.e. solutions to the SE), so that:

$$\hat{H} |\phi_i\rangle = E_i |\phi_i\rangle$$

And the lowest energy - the **true** ground state of the system- is given by E_0. Our expectation value:

$$\langle E \rangle = \frac{\langle \sum_i c_i \phi_i | \hat{H} | \sum_i c_i \phi_i \rangle}{\langle \sum_i c_i \phi_i | \sum_i c_i \phi_i \rangle}$$
$$\langle E \rangle = \frac{\sum_i |c_i^2| E_i}{\sum_i |c_i^2|}$$

Because our basis is orthonormal: $\langle \phi_i | \phi_i \rangle = 1$, and any cross terms $\langle \phi_i | \phi_j \rangle = 0$ (which justifies the summation over only variable, i).

Now, our true ground state is E_0, the lowest eigenvalue of $\hat{H}$. Then it must be the case that by construction, $E_i \geq E_0$. But is $\langle E \rangle \geq E_0$? That's what we need to prove if the VT is going to be useful. Look at the last line from above:

$$\langle E \rangle = \frac{\sum_i |c_i^2| E_i}{\sum_i |c_i^2|}$$

$E_i \geq E_0$, and $|c_i^2| \geq 0$, because the absolute value of a number squared must be positive. Thus, there is no way that $\langle E \rangle$ can be less than E_0:

$$\langle E \rangle = \frac{\sum_i |c_i^2| E_i}{\sum_i |c_i^2|} \geq E_0$$

Variational theorem proved :)

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[1] His lecture notes, if you can find them, are the chemistry equivalent of the Feynman lectures. Outstanding.

Appendix C

Hückel Reference

Energies and coefficients for various molecules tabulated here, in the event that any of the online Hückel calculators go down (or aren't accessible in China!).

Cyclobutadiene

Atom numbering goes anticlockwise around the ring.

MO Energies (increasing order)				
E_n **:**	α + 2.00β	α + 0.00β	α - 0.00β	α - 2.00β
MO Coefficients				
c_1	0.50	0.71	-0.00	0.50
c_2	0.50	0.00	-0.71	-0.50
c_3	0.50	-0.71	-0.00	0.50
c_4	0.50	0.00	0.71	-0.50

Butadiene

MO Energies (increasing order)				
E_n **:**	α + 1.62β	α + 0.62β	α - 0.62β	α - 1.62β
MO Coefficients				
c_1	0.37	-0.60	0.60	-0.37
c_2	0.60	-0.37	-0.37	0.60
c_3	0.60	0.37	-0.37	-0.60
c_4	0.37	0.60	0.60	0.37

Acrolein

Atom 4 is the terminal oxygen.

MO Energies (increasing order)				
E_n :	$\alpha + 1.91\beta$	$\alpha + 0.99\beta$	α - 0.38β	α - 1.55β
MO Coefficients				
c_1	0.22	-0.59	-0.66	-0.42
c_2	0.42	-0.58	0.25	0.65
c_3	0.58	0.01	0.56	-0.59
c_4	0.66	0.56	-0.44	0.25

Cyclopentadienyl Radical

Atom numbering goes around the ring clockwise.

MO Energies (increasing order)					
E_n :	$\alpha + 2.00\beta$	$\alpha + 0.62\beta$	$\alpha + 0.62\beta$	α - 1.62β	α - 1.62β
MO Coefficients					
c_1	0.45	-0.37	-0.51	-0.47	0.42
c_2	0.45	0.37	-0.51	0.13	-0.62
c_3	0.45	0.60	0.20	0.26	0.58
c_4	0.45	-0.00	0.63	-0.55	-0.32
c_5	0.45	-0.60	0.19	0.63	-0.07

Benzene

Atom numbering goes around the ring anticlockwise.

MO Energies (increasing order)						
E_n :	$\alpha + 2.00\beta$	$\alpha + 1.00\beta$	$\alpha + 1.00\beta$	α - 1.00β	α - 1.00β	α - 2.00β
MO Coefficients						
c_1	0.41	-0.50	0.29	-0.50	-0.29	-0.41
c_2	0.41	-0.50	-0.29	0.50	-0.29	0.41
c_3	0.41	0.00	-0.58	0.00	0.58	-0.41
c_4	0.41	0.50	-0.29	-0.50	-0.29	0.41
c_5	0.41	0.50	0.29	0.50	-0.29	-0.41
c_6	0.41	0.00	0.58	0.00	0.58	0.41

Fulvene

Atom numbering starts at the tertiary carbon, goes anticlockwise around the ring. Atom 6 is the one at the end of the terminal alkene at the top.

	MO Energies (increasing order)					
E_n :	$\alpha + 2.11\beta$	$\alpha + 1.00\beta$	$\alpha + 0.62\beta$	α - 0.25β	α - 1.62β	α - 1.86β
	MO Coefficients					
c_1	0.52	0.50	0.00	0.19	0.00	-0.66
c_2	0.43	0.00	-0.60	0.35	-0.37	0.44
c_3	0.39	-0.50	-0.37	-0.28	0.60	-0.15
c_4	0.39	-0.50	0.37	-0.28	-0.60	-0.15
c_5	0.43	-0.00	0.60	0.35	0.37	0.44
c_6	0.25	0.50	0.00	-0.75	-0.00	0.36

Phenol

Numbering as benzene, but the phenol oxygen is atom 7, attached to atom 1.

	MO Energies (increasing order)						
E_n :	$\alpha + 2.42\beta$	$\alpha + 1.85\beta$	$\alpha + 1.00\beta$	$\alpha + 0.88\beta$	α - 1.00β	α - 1.05β	α - 2.02β
	MO Coefficients						
c_1	0.41	0.17	0.00	-0.53	0.00	0.58	0.43
c_2	0.23	0.32	-0.50	-0.33	-0.50	-0.26	-0.41
c_3	0.14	0.41	-0.50	0.24	0.50	-0.30	0.40
c_4	0.12	0.45	0.00	0.54	-0.00	0.58	-0.40
c_5	0.14	0.41	0.50	0.24	-0.50	-0.30	0.40
c_6	0.23	0.32	0.50	-0.33	0.50	-0.26	-0.41
c_7	0.82	-0.48	0.00	0.29	0.00	-0.12	-0.07

Fluorobenzene

Numbering as benzene, but fluorine is atom 7 which is joined to atom 1.

	MO Energies (increasing order)						
E_n :	$\alpha + 2.84\beta$	$\alpha + 1.95\beta$	$\alpha + 1.00\beta$	$\alpha + 0.95\beta$	α - 1.00β	α - 1.02β	α - 2.01β
	MO Coefficients						
c_1	0.25	0.34	0.00	0.56	0.00	0.58	0.42
c_2	0.10	0.39	-0.50	0.31	-0.50	-0.27	-0.41
c_3	0.05	0.42	-0.50	-0.27	0.50	-0.30	0.40
c_4	0.03	0.43	0.00	-0.56	-0.00	0.58	-0.40
c_5	0.05	0.42	0.50	-0.27	-0.50	-0.30	0.40
c_6	0.10	0.39	0.50	0.31	0.50	-0.27	-0.41
c_7	0.95	-0.23	0.00	-0.17	0.00	-0.08	-0.05

Cyclooctatetraene

Atom numbering goes anticlockwise around the ring.

MO Energies (increasing order)								
E_n **:**	$\alpha + 2.00\beta$	$\alpha + 1.41\beta$	$\alpha + 1.41\beta$	$\alpha + 0.00\beta$	α - 0.00β	α - 1.41β	α - 1.41β	α - 2.00β
MO Coefficients								
c_1	-0.35	-0.35	0.35	-0.50	-0.00	-0.35	0.35	0.35
c_2	-0.35	-0.50	-0.00	0.00	0.50	0.50	0.00	-0.35
c_3	-0.35	-0.35	-0.35	0.50	-0.00	-0.35	-0.35	0.35
c_4	-0.35	0.00	-0.50	-0.00	-0.50	-0.00	0.50	-0.35
c_5	-0.35	0.35	-0.35	-0.50	-0.00	0.35	-0.35	0.35
c_6	-0.35	0.50	0.00	-0.00	0.50	-0.50	0.00	-0.35
c_7	-0.35	0.35	0.35	0.50	-0.00	0.35	0.35	0.35
c_8	-0.35	0.00	0.50	0.00	-0.50	0.00	-0.50	-0.35