

## MITOCW | MIT3\_091F18\_lec12\_300k

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And speaking of VSEPR, that's what we did last lecture.

We're going to move on today.

But I want to just clarify something about VSEPR.

When I was talking about this I tried to put two different concepts in the same place.

And I put something in the table that shouldn't have been there.

And people corrected me.

I want to be sure that there is no confusion around this.

So what we had was a case of formaldehyde.

And we had the case of  $\text{SO}_2$ .

And I want to be really clear about this.

Both of these molecules, when you're thinking about VSEPR, the number of electron domain count--  
Right.

Remember, that's how we start.

The number of electron domains is the same for both of them.

And we did this on Wednesday.

Right.

And if the number of electron domains is the same, then the electron domain geometry is trigonal planar.

Right.

OK.

But I was also telling you about repulsion order at the same time.

And so I put the wrong thing in the table.

And then I erased it.

And I just want to be sure we're clear and we don't get bent out of shape about it.

[LAUGHTER]

Stop.

[CLAPPING]

Get out of here.

Stop.

Stop it.

All right.

All right.

I'm going to still be here.

I'm going to be here.

All right.

So like here, right, the shape.

Remember, what the table was about was the number of lone pairs.

OK.

The number of lone pairs.

And so if I've got the three binding pairs and no lone pairs, then it's going to be a trigonal planar shape.

So that is trigonal planar.

And over here I've got two bonding pairs and one lone pair.

And so this shape is called bent.

Now, what I did is I used that word.

Aw, why?

I don't know.

But you make mistakes.

When you're in the arena, you keep going.

And if you make a mistake, you admit it.

You leave it all there.

You do your best.

Forget the rest.

That's all you can ever do.

Now, here's the thing.

I said bent.

I said the word bent.

And what I was talking about was how that bends a little bit because of the repulsion order.

Yeah.

But that shape is not bent.

I want to be real clear about that.

That shape is trigonal planer.

And it's a little bit distorted.

OK.

This shape is bent.

That shape is bent, because it's got a lone pair.

Remember, the shape is about where the atoms are.

But it's also a little bit distorted.

Right?

Because the lone pair pushes on those guys a little bit more.

All right.

OK.

So those are the two concepts that I was saying all at once.

And I want to make sure we understand them.

There's trigonal planar.

there's bent.

And then there's repulsion order, which talks about little changes in the angle from those parent shapes.

OK.

Good.

All right.

Now, onto today.

Now, here's the thing.

Now, in all of this stuff with Lewis, it's a really good way to think about molecules.

But this tells me that there's electrons on the bond.

It tells me that there's electrons really localized in the region between the atoms.

But see, the thing is, how much is it localized?

How much is it really?

Are these electrons-- if I were to draw the two electrons, are those dots right there?

It doesn't really tell me more information than that.

But if we remember the picture-- let's see if I can pull.

Yep.

There it is.

There's a picture I showed you when we first talked about covalent bonds.

Sharing is caring.

Remember what happens.

I've got the two protons.

And we talked about these.

A repulsion.

And then the two electrons.

Repulsion.

And then I drew for you the fact that, but they can come together.

And they can be like, you know what?

You can use my proton for a little of your attraction.

And hey, can I use your-- And they share it.

And each electron sees both of them.

And this is where those electrons are.

But look at that.

The proton is there and there.

And the electron is in this probability cloud around both of them.

That's the molecular orbital.

And Lewis can't tell us about that.

So we need something else.

And that's what today's topic is about.

Today we're going to talk about something called molecular orbital theory that gives us a sense of how these atomic orbitals overlap.

It gives us a much better and a deeper description with more details about these covalent bonds.

OK.

All right.

Now, so let's write a few things about molecular orbital theory.

Molecular orbital.

And what we're going to do is say, MO, and Molecular Orbital theory.

So we'll keep a list of some important things.

All right.

Well, first of all, the first thing is that atomic orbitals, or, as we may call them, AOs, are the basis for-- watch this efficiency, the MOs.

I didn't have to write it again.

Right?

OK.

So what does that mean?

Well, it means that I'm going to construct the MOs from the AOs.

Now, the AOs are the things we've been playing with and making.

Right?

We solved the Schrodinger equation.

So the MOs are going to be linear combinations.

All right.

Combinations of the AOs.

And that's why you might see this, in fact, called LCAO theory.

LCAO.

Linear Combination of Atomic Orbitals.

OK.

And in particular, sum and difference of orbitals is what we're about.

Because this is like what we talked about before.

These are waves.

Right.

These are waves.

Waves can either constructively or destructively interfere.

And that's what we're going to explore in MO theory.

By adding or subtracting these wave functions, these orbitals, these atomic orbitals.

So that's enough to start.

Let's see.

So look, basis.

A basis is nothing more than the things that I'm going to use to represent the things that I want.

Right.

And the things that I want are these molecular orbitals.

And the things that I'm going to use to represent those are these, these beautiful atomic orbitals that we spent a lot of time understanding and developing.

We'll start with the simplest case, which is-- I think I have-- oh, I even highlighted it.

And I said, let's first make molecular orbitals using combinations of the S orbital.

That's the S orbital.

That's the 1s orbital up there.

Remember, by the way, blue and orange is just the sign of the wave.

Right.

This is not a charge.

Please don't make that confusion.

These are just waves.

Right.

Waves.

And let's go back and see it.

The p orbital has a plus and a minus.

It's a wave.

All right.

And the 2s orbital has that too.

And then you square it, and you get the probabilities.

Right?

OK.



So we'll start with 1s where it's all just one sign.

And I can add it.

I can add an S and another S. Or I can subtract it.

So let's do that.

Right.

So we'll do that over here.

All right.

So if I take a 1s orbital, and I add it to another 1s orbital, well, you can see, as I bring these close together, if they have the same sign, these are waves.

So if the waves are both positive, and I bring them together, they can constructively interfere.

So as I bring them closer and closer, well, I might actually get the picture that I showed you, right?

I might actually get something that looks like this.

OK.

I might actually get something like this.

Now, if I subtracted them, then as I bring these orbitals closer together, well, they're going to cancel each other.

And you can see right here, if I bring these orbitals-- by the way, which are coming from two different atoms.

Right.

The whole point is we're talking about molecules, molecular.

So if I bring them together now like this, but I'm subtracting these orbitals, then you can see that right at the interface, right between them, it's always zero.

Because I've just subtracted the same amount.

No matter how close they get, it's zero.

That's a node.

Right.

And, in fact, what you're going to get is something that looks like this.

Now, so what I've done is I have added and subtracted the same AO.

And I've created two MOs.

So these are my MOs.

And these are my starting AOs.

That's about the simplest thing you can do in MO theory.

So I'm using these as a basis.

Now, there's something very important, which is that-- I kind of already alluded to this-- these are two atoms coming together to make a bond.

This is the bonding axis.

This is the bonding axis.

OK.

Now, if an orbital, if an MO is symmetric, so if it has cylindrical symmetry about that bonding axis, then it's called a sigma orbital.

It's called a sigma orbital.

That's the MO.

Sigma is a notation.

A sigma orbital is one that has symmetry around the internuclear axis, the two-- Does Pauli exclusion not apply to that?

We're coming to that very soon.

Because these are just the orbitals.

I got to do something with them.

It's just like over here.

I made all these orbitals.

But then I had to fill them.

That got me excited.

But you can see right here.

When I add them up there's charge in between.

So this looks like it's going to have a bond.

That's a bonding MO.

But if I subtracted them, this doesn't look very happy in terms of electrons being in between and the caring is sharing principle of a covalent bond.

Right.

So if I were to put an electron in this MO, it doesn't look bonding.

In fact, it looks-- Non-bonding.

Or antibonding.

It's actually not quite non-binding.

We'll get to that later.

This would be antibonding.

Why?

Because there's not even a chance of electron density in between.

That's your starting principle of the relationship.

Let's try to share.

Oh, by the way, right half way, no chance.

That's not a very good way to start.

And you can see why this is antibonding.

It's the opposite.

You're actually pushing charge away from the bond if you're an electron in that orbital.

So that's an antibonding orbital.

Now we get to the question.

What do you do with these orbitals?

Well, you make them.

I made these with 1s.

And the way that we typically draw this is we go back to the same picture that we've been working with, 1s here and 1s here.

And I brought those orbitals together, and I formed one that lowered the energy of the system, and another that actually raised the energy of the system, because the electrons are repelling.

They're actually less bonding.

They're antibonding.

All right.

So these are my MOs.

Those are my AOs.

Right.

AO, AO.

And now, this is called a sigma orbital.

And the way we refer to the antibonding orbital is with a little star.

They're both sigma because they both satisfy that.

Right.

They're both sigma cause they both have symmetry around the inter nuclear bonding axis.

But now, see, OK.

So that's good.

But now let's fill them.

Let's fill them.

Because now let's write down the rules.

And then we'll fill them for some examples.

OK.

So I'm going to keep going on my MO theory list.

Right.

As you can see, when I do it this way, the number of MOs equals the number of AOs used to create them.

So that's one thing that we can see right away.

Right.

I used two AOs.

I added and subtracted them.

I got two MOs.

That's good.

Well, another thing is, each MO will be just like an AO.

It makes a lot of sense.

I had room for two electrons here.

I had room for two electrons here.

I got to have room for four.

Two here.

Two here.

Right.

So each MO has a max of two electrons.

And they must obey Pauli, just like in AOs.

They must obey Pauli.

You can't mess with quantum mechanics.

Uh-uh.

They're still electrons.

They're still quantum mechanical.

All right.

You're just making their wave function more sophisticated.

But they still have to follow the Schrodinger equation and the principles of quantum mechanics.

And so, finally, what we're going to do is we're going to fill them.

So we're going to fill the MOs with electrons, starting with the lowest energy, just like we did for atoms, lowest energy first.

OK.

And one more thing.

Just like we did with atoms is we're going to obey Hund.

Hund.

Hund's rule, which tells you about how to fill degenerate orbitals.

Well, we're going to have degenerate orbitals here too.

We don't yet.

But we will.

So we're going to fill them.

So let's fill them for the very simplest cases.

OK.

So we'll do some cases together.

And we'll see how that goes.

All right.

So what I'm going to do are four cases just so we can compare.

So first, we're going to do  $H_2$  plus.

OK.

That's the first one.

And here, what we have is the same graph.

But now, over here I actually can label it now.

This was just an orbital.

But now, gazuntite.

Now, I'll say, OK.

Well, this would be like  $H$  and  $H$  plus.

OK.

These are my MOs, sigma, sigma star, 1s, 1s.

Oh, boy.

So if that's H and that's H plus, and they're coming together to make H<sub>2</sub> plus-- that's what's in the middle there.

That's the molecule.

All right.

Well, then I also can now fill in the starting AOs.

So let's do that.

That's it.

Because somebody had to lose an electron to start with.

So now, when these come together, you fill.

You obey the Pauli exclusion.

You fill it from the lowest energy first.

You say, well, I only got one electron.

There it is.

That's my MO diagram populated by electrons.

OK.

Now, there's a principle that comes out of this.

There's a way of understanding bond strength now.

There's a way of understanding bond strength.

And that is a very important concept.



Now, let's put it here in our list.

OK.

And it's a concept called bond order.

Now, this one I really want to write BO.

But I don't know if that's a good idea.

I got Laura on that one.

OK.

And there's a definition for this.

It's going to equal  $1/2$  of the number of electrons in a bonding orbital, minus the number of electrons in an antibonding orbital.

Sorry.

This is a little bit small here.

But we'll do a bunch of them so you can see what this means.

Right.

So now, the bond order is important because the bond order of a molecule, if it's higher than a stronger bond, and it has to be greater than zero for stability.

Let's see how that works.

And we'll see this intuitively as well as we fill these up.

Right.

So if I count the bond order here-- oh, I'm going to do it.

I don't feel like writing it out.

The BO on this one is  $1/2$  times  $1$  minus  $0$ , which equals  $1/2$ .

OK.

Good.

It's  $1/2$ .

Well, it's greater than 0.

So right away I know that the  $H_2$  plus molecule is probably stable.

That's good.

But let's go to some more examples now.

Let's do a few more.

All right.

Now we're going to work our way to  $H_2$ .

And in this case, energy is always going up in these diagrams.

Now, each of these H atoms is bringing an electron.

There's no charge to the system.

And so now different quantum numbers.

Pauli.

But same sigma.

Right.

And so now that's the  $H_2$ .

Now, the bond order here is equal to 1.

Right?

I didn't have any electrons in an antibonding orbital.

All right.

But you know what's coming.

I'm going to do He<sub>2</sub> plus next.

And let's just put it here for comparison in real time.

If I were He<sub>2</sub>, each of these would be the AO occupation of an He atom.

Right?

But since I'm He<sub>2</sub> plus, one of them is missing an electron.

So this is what you're going to see.

These are both He atoms still, but one of them is plus in this picture.

But see now, OK.

I've got three electrons.

They're going to go here.

And I've got to put one up here.

I have to.

Cause I had three.

I got to keep on filling, just like in an atom.

But now I'm filling bonding and antibonding orbitals.

All right.

And here I've got this and two up there.

So if you look at the bond order, here the bond order is still positive.

Here the bond order is zero.

And, in fact, that's why He<sub>2</sub> is not a stable molecule.

Because you're putting just as much charge on this thing that wants to bond it as you are on this thing

that doesn't want to bond it.

And at the end of the day, it leads to a molecule that is not stable.

So that would be He<sub>2</sub>.

But He<sub>2</sub><sup>+</sup> has a bond order that's similar.

Did I get something wrong?

He<sub>2</sub><sup>+</sup> plus 1/2.

OK.

Now, because this weakened it.

Right.

This weakened the molecule, compared to this, because now I added charge to an antibonding orbital.

So you would expect from the bond order that this one is more stable than this.

And, in fact, that's what you find.

Right.

The H<sub>2</sub> molecule has a stronger bonding energy.

Now, we can write the molecular orbital configurations just like we did with the atomic orbital configurations.

OK.

And so like for here, so for this case-- I'm going to write it up top if I can fit it.

So here we would have sigma 1s.

And we're populating it with-- Ah.

That's not my example.

[GRUNTING]

This is my example.

Sigma 1s is the orbital.

And we're populating it with one electron.

Right.

So that's how we would write that.

Now, if we go to the next examples, we would have this one is this molecule you would write as sigma 1s 2.

So this would be sigma 1s 2.

And oh, now I've got sigma 1s 2.

Oh, this is getting interesting.

Because now it's sigma star 1s 1.

So everybody see that?

I populate.

This is just like SPD.

But now I'm just filling those MOs up.

And I'm showing you what the molecular configuration is with those molecular orbital names.

Sigma 1s.

Sigma 1s star.

OK.

Good.

Now, we can keep going.

We could do this all day.

Actually, we kind of will.

But we're going to move on-- don't worry-- from sigma.

Let's see.

Let me go over here.

There's another concept that I want you to know about MO theory.

So if I kept going, I could have, for example, let's do lithium.

OK.

So now, lithium 1s.

Oh-ho.

2s.

Lithium brings this.

What does it bring?

It brings three electrons.

And over here, 1s and 2s, three electrons.

So this would be the lithium dimer.

But I want to make an important point.

When you would draw this one, here's how I would draw it.

Whereas when I would draw this one, I would draw it like this.

OK.

Now, those are supposed to be the same spacing.

I'll tell you in a second.

Notice that the distance here between the bonding and antibonding orbital is larger than it is here.

The reason is because it's related to the overlap.

So there's another point, which is that the overlap of AOs is related.

So the greater the overlap of AOs, the greater the change in energy between bonding and antibonding orbitals.

And let's be clear.

Those are molecular.

But see, you could see like, if I'm lithium, those 1ses aren't going to overlap too much.

Right.

They're kind of close to the core.

So you do get MOs there.

But the difference that you get depends on how much these electrons are near in energy and overlapping.

All right.

So the 2s can overlap a lot more.

OK.

Now, if I were to fill this up, we would get something like this.

These sigma 1ses-- oh, sigma 1s.

What do you think these are called?

2s.

Sigma 2s.

Sigma 2s.

Sigma 2s.

OK.

This is getting a little bit-- I'm going to draw this out here.

That's the sigma 1s star.

Right.

And this would be the sigma 2s star.

Well, what am I going to occupy?

Well, how many electrons do I have to pour into the molecular orbitals?

[GRUNTING]

Lithium 2 is stable, because its bond order is-- you see.

Bond order.

Number of electrons in bonding orbitals, one, two, three, four, minus the number of electrons in antibonding, minus 1, 2, divided by 2.

So the lithium dimer bonding order is 1.

All right.

And then you can go on, and you could say, well, if I had beryllium, I'd have another electron here and here.

And I'd fill those antibonding orbitals up again, like in the He<sub>2</sub> dimer.

And I would have, again, an unstable molecule, which is, in fact, true.

OK.

This is sort of the simplest way you can think about molecular orbital theory because it's the simplest orbital.

But you could spend the whole night.

And it is a Friday.



What else do you have-- this is what you do on a Friday.

After I watch Dr. Quantum I'm going to just add every single one of these with every single one.

It's finite.

It's not going to take forever.

Let's just do p.

OK.

Now, with p orbitals there's something interesting that happens, because now that sign-- you see how the p has a plus and a minus?

Right.

And so you've got to kind of think about that a little bit.

OK.

If I take a p orbital, and I'm going to do it like this.

Minus, plus.

And I'm going to add it to a p orbital that looks like this.

And notice, I'm taking these and I'm adding them along an axis where they're kind of both along the axis.

Right.

They're both along the axis.

And by convention, we'll do the p<sub>z</sub> as the one along the axis.

Remember, there's p<sub>x</sub>, p<sub>y</sub>, and p<sub>z</sub>.

When we solve for the p orbitals, those are the M<sub>s</sub>. Those are the M<sub>s</sub>. Right.

One.

Zero.

And minus 1.

Now, by convention we put the p<sub>z</sub> along the bonding axis.

And you can see right away, so if I do this, well, I'm going to start adding these wave functions constructively.

And what you're going to get is-- let's see if I can draw this-- something that looks like that.

And where this is actually going to be plus.

And this is minus.

And notice that I'm going to have nodes in there.

Right.

I had nodes in the original orbitals.

But I got a lot of bonding in between.

I got a lot of bonding density in between.

That is a bonding orbital.

And the other thing we see about this is that it is symmetric around that bonding axis.

So it's actually a sigma p<sub>z</sub> orbital.

It's a sigma.

We call it a sigma, because it's symmetric around the bonding axis.

Now, if I were to take a p<sub>x</sub>-- oh, well, let's actually subtract these.

OK.

So minus, plus, minus.

Now, what you see is something very different, right.

So now, oh, boy.

Can I draw this?

Maybe.

I don't know.

OK.

I'll take that.

Right.

And so now what you see-- so I'm subtracting these.

And so the density goes down.

And now, you're going to get minus, minus.

Right.

Plus, plus.

But I've reduced the electron density.

And even worse, I'm back to that situation where right in between where I want to share the most, I'm saying no.

No probability density there.

And that's an antibonding sigma p orbital.

So this would be sigma star pz.

OK.

Sigma star pz.

Now, the other thing that you can do is look at the other directions.

Right.

And so I'll just take one of those really quick.

And if you do that, you see something different.

All right.

So now, let's combine these like this.

By the way, some textbooks.

We're adding and subtracting.

We're constructively interfering and destructively interfering.

So sometimes you'll see a textbook add like this, or add the other way, which is subtracting like this.

But it's the same thing.

Right?

You can decide how you want to orient it.

But we're adding and subtracting constructively and destructively.

That's what we're doing.

So I'm going to choose to add it like this.

Because then you just see, if I do this, then those are going to have some kind of overlap.

Right.

Those are going to have some overlap of plus appear and some overlap of minus down there.

And that is called, oh, a pi orbital.

Yeah.

Yeah.

But if I subtracted them, then what you would see is something that looks more like this, where you got that node in between again.

Right.

And this would be a pi star orbital.

This would be for like px orbitals.

Now, notice, these cannot be sigmas, because the pi orbital is not symmetric around the bonding axis.

OK.

These cannot be sigmas.

But that's why we have another symbol for them.

Luckily, we've got a lot of symbols, and the chemists are geniuses at naming things.

And so these are called pi orbitals.

And as you can see, OK.

I have three orbitals.

One, I put it along the axis.

And then I've got two going perpendicular in the other plane.

And this is one of them.

And then the other one would be the other one, py.

So as you can see, I'm going to have a sigma star, two pi orbitals, and two pi star orbitals.

Right.

And then what we got to do is we got to put them on our energy scale.

And instead of going through drawing it all, I'll save myself a few minutes here.

I'll show it to you.

All right.

So there is that energy scale.

And oh, they're pointing out the nodes.

Isn't that beautiful?

You can see right here.

They're not saying what molecule this is yet.

This is a 2p orbital.

And it's pointing along the same bond axis as the other one.

So this is going to be a sigma p orbital.

This is a sigma p orbital.

And you can see that.

And there's a sigma star.

Right.

Good.

Now, if we go to that, there's the next one.

There's a pi orbital.

And you get the same exact effect.

You've got a lowering of the energy, cause you're putting electrons on the bond, and a raising of the energy cause you're taking them away.

Right.

And that's what it looks like for the pi orbital.

And we can put it all together.

And if you put it all together, what I want to do is put it together for O<sub>2</sub> and then show you a video, and then do my why this matters.

Now, if you put this together, I'm going to show you the system for oxygen and nitrogen. OK.

And then we'll do a couple other cases too.

But we're going to do oxygen first.

So if I take oxygen, then I'm not even going to write 1s anymore.

That's way down in energy.

It's not really involved in the bonding.

I'm going to leave it out.

But I've got my oxygen 1s, oxygen 1s.

OK.

Good.

So those are going to come in and form molecular orbitals like that.

And we know that they are all filled.

OK.

Now, up here I've got my oxygen. Sorry.

I just said I wasn't going to do 1s.

And I'm not.

Those are 2s.

Those are 2s.

Sigma 2s.

Sigma star 2s.

OK.

Good.

All right.

Oh.

Let's see.

Now, over here, I start with my ps.

And I start with px, py, pz.

And in oxygen, how many electrons do I have in here?

So it's like this.

[INAUDIBLE]

Everybody should be shouting.

[SIGHS]

That's so much better.

That was close.

And then I've got to-- well, I'm not going to have enough room.

I've got these over here.

px, py, pz.

Ha, ha, ha, ha.

And there is oxygen.

But you see, now, they come together.

And they form these MOs.

And we just went over what types they are.

Right.



There's a sigma pz orbital.

And there's a sigma M. But the ordering is about the same thing that we learned, which is that it has to do-- this delta is up there.

This delta is up there.

And so in that pz for oxygen, you can overlap more.

It pushes those apart more.

And so what you get is that the pis are inside like that.

The pis are inside.

Right.

So if I write in here, it's going to get too small.

So I'm going to do this.

This would be a sigma 2pz.

This would be a sigma 2pz star.

And over here, these would be pi orbitals.

Pi px, pi py.

And these almost can fit pi star px and pi star py.

All looking like the shapes that we've been drawing.

Right.

And then the filling part comes from the filling of the AOs.

Right.

I've got my filling of the AOs here.

I've got the valence filling for oxygen.

There is a 1s down there.

Right.

And so I've got to put four electrons from there and four electrons from here into the middle.

So let's do that.

One, two, three, four, five, six, seven, eight.

Pauli.

Pauli.

Right.

So for oxygen, the bond order, if you add it up, the BO is two.

It's a double bond.

We know that.

Oh, but now we know so much more.

And this is what I want to make a point.

Lewis could have gotten us this.

But Lewis can't get us magnetism.

Lewis can't get us magnetism.

Molecular orbital theory can.

OK.

And let me show you magnetism right up close.

Because if I take liquid nitrogen. That's not me though.

And I pour it through a huge magnet.

I want that magnet so badly.

But if I did that, look at that.

Liquid nitrogen just goes right on through.

And it's really fun to do actually.

But there you go.

That's liquid nitrogen.

But look at liquid oxygen. Liquid oxygen. Now you pour it through, and the magnet holds it in place.

All right.

Whoa is right.

There's four more things we've got to cover.

One is paramagnetism.

Another is something called mixing.

Another is what happens when you go hetero nuclear.

Oh, yeah.

You'll see what that means in a second.

And finally, what I said I would get to, which is non-bonding, which are not the same as antibonding.

What I'm covering right now, there, is paramagnetism.

Because as you saw on the exam in one of the questions, we explained it.

We said if you got unpaired electrons, then you are-- what does paramagnetism mean?

It means that if you put a huge magnet on it, you'll respond.

You will feel a force from that magnetic field.

And so we did that in the exam.

We had a silicon atom, because we hadn't done molecules.

But now we got molecules.

So I can tell you why that experiment happened.

What's happening?

I can tell you why that experiment happens.

Really?

I didn't even know there was more.

[LAUGHTER]

It happens because of Hund's rule, molecular orbitals, and the fact that I've got these two unpaired electrons in the O<sub>2</sub> molecule.

And you know that in nitrogen those two electrons are gone, cause nitrogen is missing one more here and here.

So you've got two less.

Everything's filled.

Everything's filled.

Paramagnetism.

Now, OK.

Speaking of magnetism, I couldn't help but show you this.

This is diamagnetism.

Now, diamagnetism, everything is filled.

But you still feel a little repulsion to a magnetic field.

And some of you may know there is this thing called the Ig Nobel Prize.

Only one person in history has won both the Ig Nobel and the Nobel Prize, Andre Geim who discovered

graphene with scotch tape.

But before that he won the Ig Nobel Prize because he did this to frogs.

Because water is diamagnetic.

And so it repels a magnetic field.

It's just got to be really, really, really high.

I hope that frog was OK.

It looked sort of OK.

So the frog was floating.

And it was like a study about levitation using magnetism.

Why am I showing that to you?

No particular reason.

[LAUGHTER]

But this does get me to the why this matters, which has to do with how you cook pasta.

And, of course, since we're talking about O<sub>2</sub>, when I have finished cooking pasta, what do I do?

I pour it.

There it is.

It's like it's sophisticated.

I pour it through a colander.

That's a membrane.

That's a membrane.

You did use a membrane.

You did a filter.

Now, but I could also have done that separation, that same separation, I could have left it on the stove.

I could have.

And it would have boiled out all the water and left me still with the pasta separated from the water.

I've accomplished the same exact thing.

I have separated the pasta from the water.

Test done.

Pasta may not taste as good.

[LAUGHTER]

But you've done it.

But see, the thing is that if you separate things this way versus that way, you can just feel how much less energy it's going to take.

In fact, you can save over 80% of the energy if you do a membrane based separation as opposed to a thermal one.

Gazuntite.

So those are two ways to separate pasta.

But see, there's two ways to separate lots of things.

Like how about 1 to 10 nanometer particles?

How about chemistry?

How about molecules?

How do you separate those?

Well, you got the same two ways.

And if you count up all the things we separate this way, it's a lot.

It goes on and on.

And it will go all the way down the Infinite Corridor.

And this is how we do chemistry.

In fact, has anyone seen this on the side of the road?

That's a distillation column.

It's a big pasta cooker.

That's all you're doing is boiling one molecule off of another over a long time with a whole lot of fossil fuel.

In fact, if you look at the US energy consumption, roughly a third of it goes into industry.

40% of that is for this one thing.

It's boiling pasta.

But the pasta is 1 nanometer to 10 nanometer particles.

40% goes into boiling one chemical species off of another.

Separation.

Separation.

That's 12% of all the energy.

That's the same as every single drop of gasoline in every single car truck and bus.

Just to give you a sense of how much energy that is.

You'll say, well, why aren't we using a colander?

Why don't we just pour it through a colander like we do our boiling pasta?

Well, we do that for one field.

Desalination.

I got a [INAUDIBLE] on that another time.

But we don't do it for all those other things.

And there's a really simple reason.

We don't have the right pasta colander.

We don't.

There's no option for that size scale that can withstand the conditions that are in all of those chemical separations.

But if we did-- we take so much O<sub>2</sub> out of the air.

We need O<sub>2</sub>.

But we don't want the N<sub>2</sub>.

So we have to separate it.

How do we do it?

We go cryogenic.

We go to very, very cold temperatures, which is the same as boiling.

Right.

But you're still spending all this fossil fuel to lower the temperature.

That's how much O<sub>2</sub> we generate each year.

And this is how much energy it takes.

It's like 1/2 a percent of all US energy, just to get-- But what if you could use something like O<sub>2</sub>'s paramagnetism?

What if you could use something about the chemistry of O<sub>2</sub> to do this separation more efficiently, lower energy, or maybe make a new colander that does that?

And if any of you have ideas, come talk to me.



This is a problem I care a lot about.

OK.

Ah.

But I had some other-- paramagnetism.

Unpaired electrons.

We got that one.

Ha.

[SIGHS]

Why is chemistry not-- why can't they follow the rules?

Why?

But they always got to break them.

And what we see, this was oxygen. Sigma.

Sigma S. Sigma.

Sigma star.

Pi.

Pi star.

But look at what happens for nitrogen. Why?

Because of something some people like to call mixing.

Remember, I said that-- where did it-- somewhere I said that the closer in energy, or the closer in symmetry orbitals are, the more overlap they can have, and the more they interact and can mix together in the ways that I've been talking about.

Yeah.

Well, it turns out that if you go below oxygen, in what are called homonuclear dimers, which is where the atoms are the same, then you can get mixing even between this sigma and that sigma.

And so what happens is, instead of them being kind of separate like this for N<sub>2</sub>, there is an interaction.

You see.

You can think about it the same way.

I'm throwing more orbitals into the mix.

And so because they can contribute to overlapping, you're changing that delta E even more.

That's effectively what's happening.

And so you can see this one for nitrogen goes down, but that one goes up.

Because that's the delta E. Because it's able to mix in.

It's able to mix in because they have the same symmetry.

And they're closer.

For those smaller atoms, they're a lot closer in energy.

And so if you look at this, what happens is those switch.

They switch.

It's real.

They switch.

Now, it doesn't change the thing I just talked about, which is the magnetic properties of N<sub>2</sub>, because they are still all filled.

But it is important.

Because if I were to pull an electron out of N<sub>2</sub>, it would come from a sigma orbital, not a pi orbital, because of those interactions.

And those happen below O<sub>2</sub>.

So this is from your textbook.

And you see, it says 2s 2pz interaction.

Remember, 2pz is sigma.

Sigma.

Same symmetry.

Able to mix.

Don't mix very well here.

But here they're strong enough to change the ordering of that orbital and that orbital.

Right.

You see that?

That's an important effect.

OK.

All right.

But it only happens below O<sub>2</sub>.

It happens below O<sub>2</sub>, because that's where those energies and orbitals can line up in that way.

OK.

So we just covered that.

Now, there's two more things.

And then that's all of MO theory.

One is I've been giving you the same atoms.

But what if we go from a homonuclear dimer to a heteronuclear dimer, which just means one is one

and one is another type of atom.

How do we draw an MO diagram for that?

And the second thing is what happens?

The second thing is what happens in this case?

In HCl, H is bringing only one S electron to the party.

But Cl is bringing all of the-- it's bringing S. It's bringing P. What does it do?

Right.

How does the MO diagram look in that case, where I've got all these extra electrons coming in from one of the atoms.

Now, I will not do this in 30 seconds.

But I will, next week, give you a nice sort of thorough explanation for each of these two last MO cases.

In the meantime, have a very good weekend.