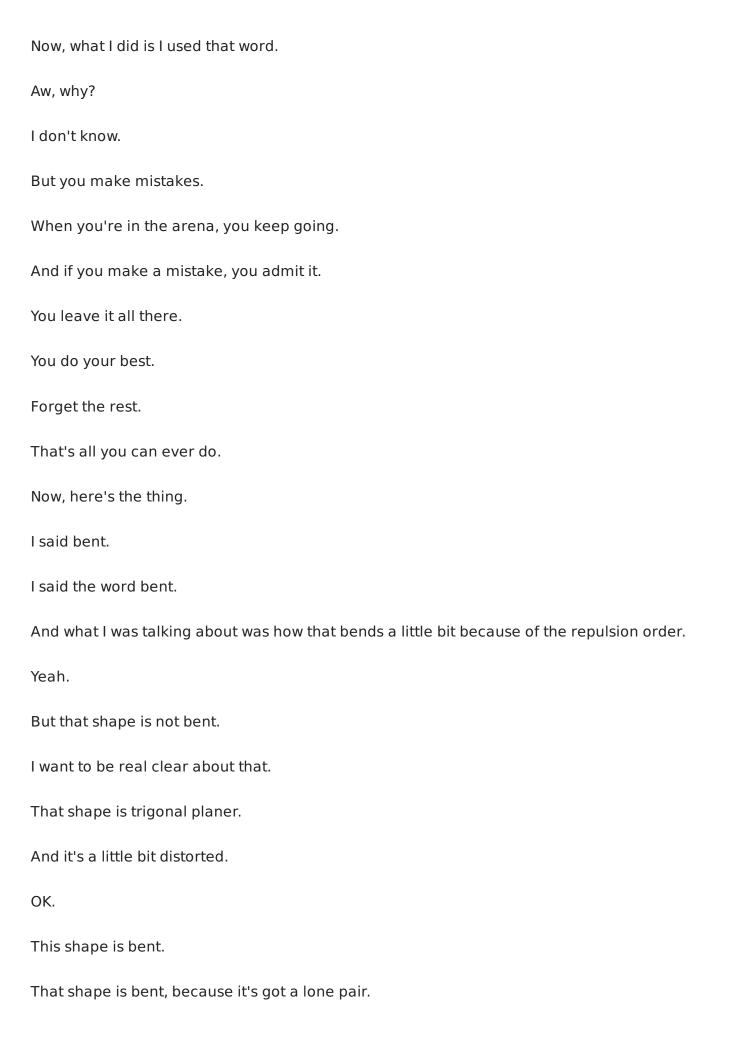
MITOCW | MIT3_091F18_lec12_300k And speaking of VSEPR, that's what we did last lecture. We're going to move on today. But I want to just clarify something about VSEPR. When I was talking about this I tried to put two different concepts in the same place. And I put something in the table that shouldn't 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 SO2. 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.

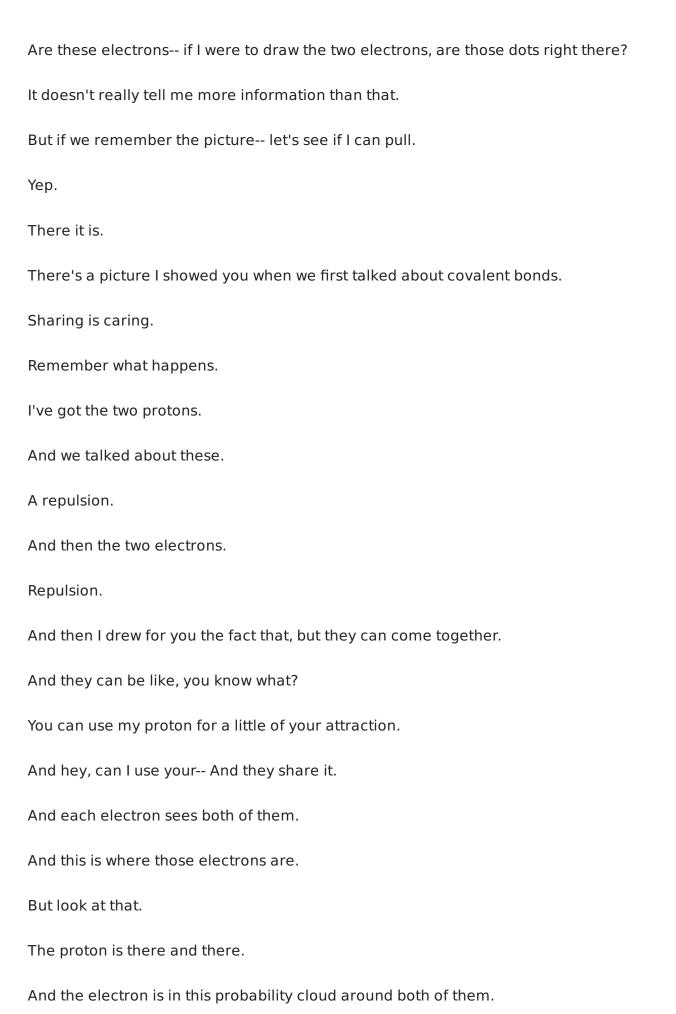
But I was also telling you about repulsion order at the same time.

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.



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?

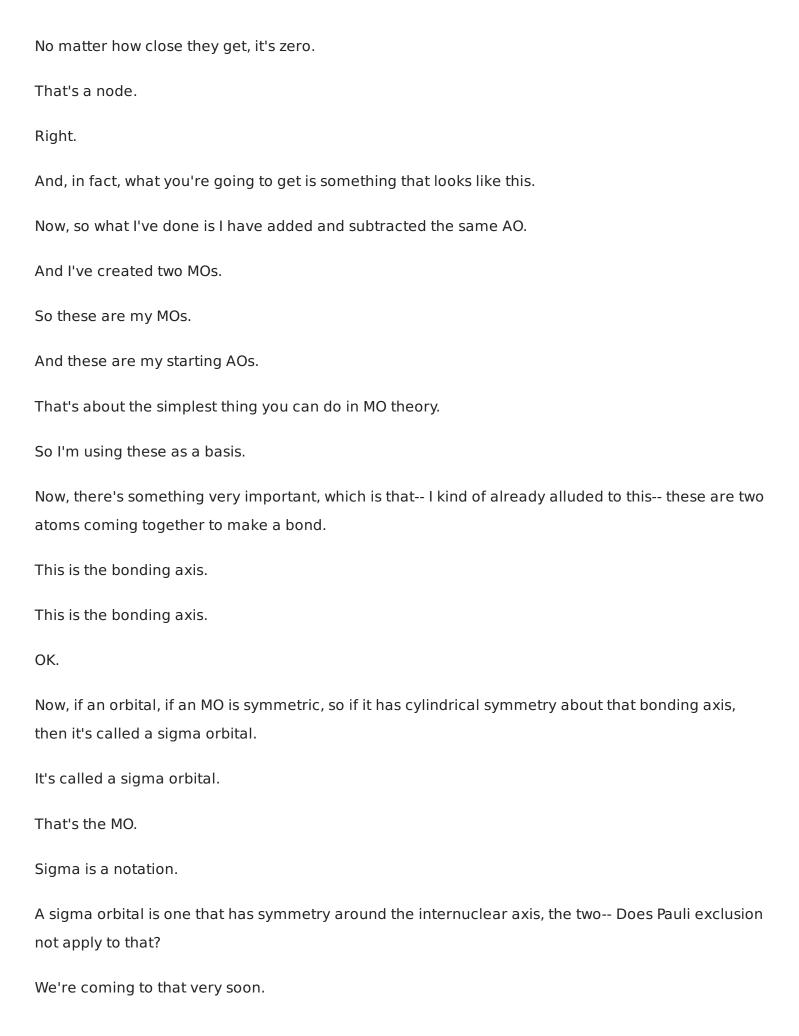


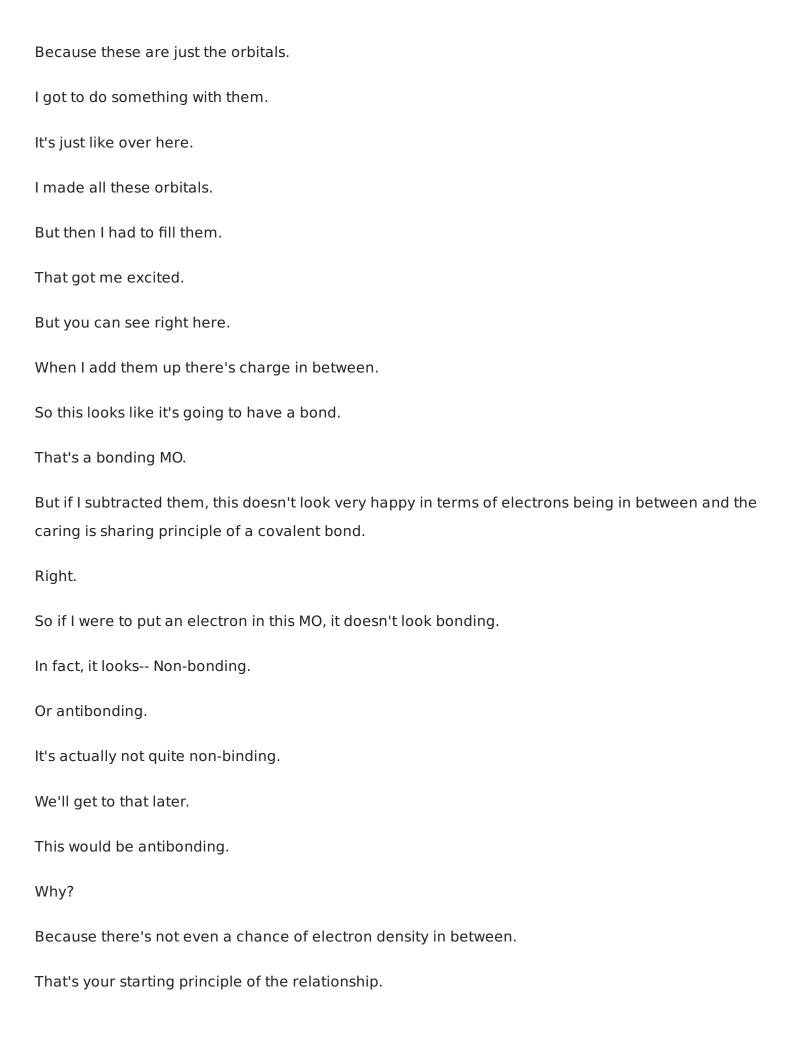
That's the molecular orbital.
And Lewis can't tell us about that.
So we need something else.
And that's what today's topic is about.
Today we're going to talk about something called molecular orbital theory that gives us a sense of how these atomic orbitals overlap.
It gives us a much better and a deeper 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 forwatch 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.



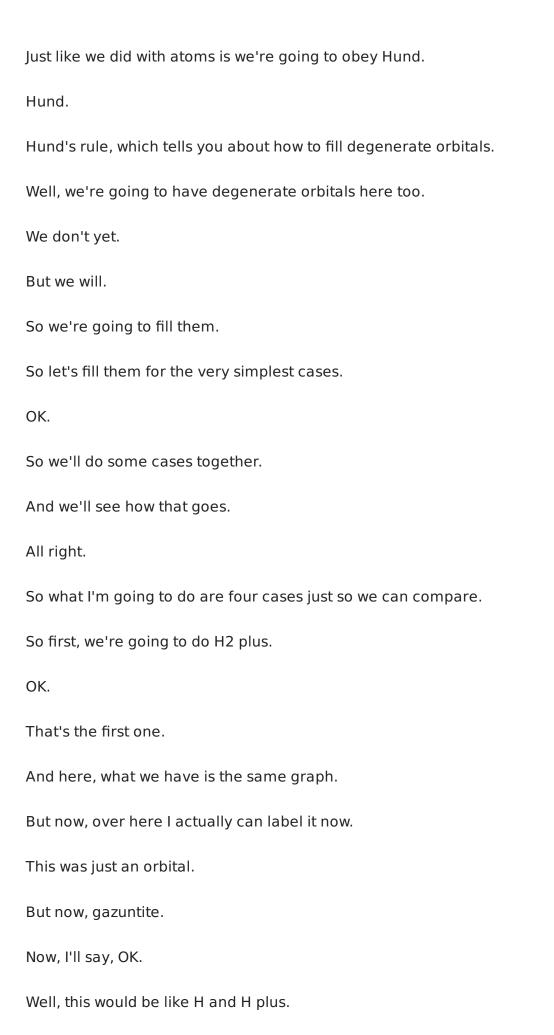




Let's try to share.
Oh, by the way, right half way, no chance.
That's not a very good way to start.
And you can see why this is antibonding.
It's the opposite.
You're actually pushing charge away from the bond if you're an electron in that orbital.
So that's an antibonding orbital.
Now we get to the 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.

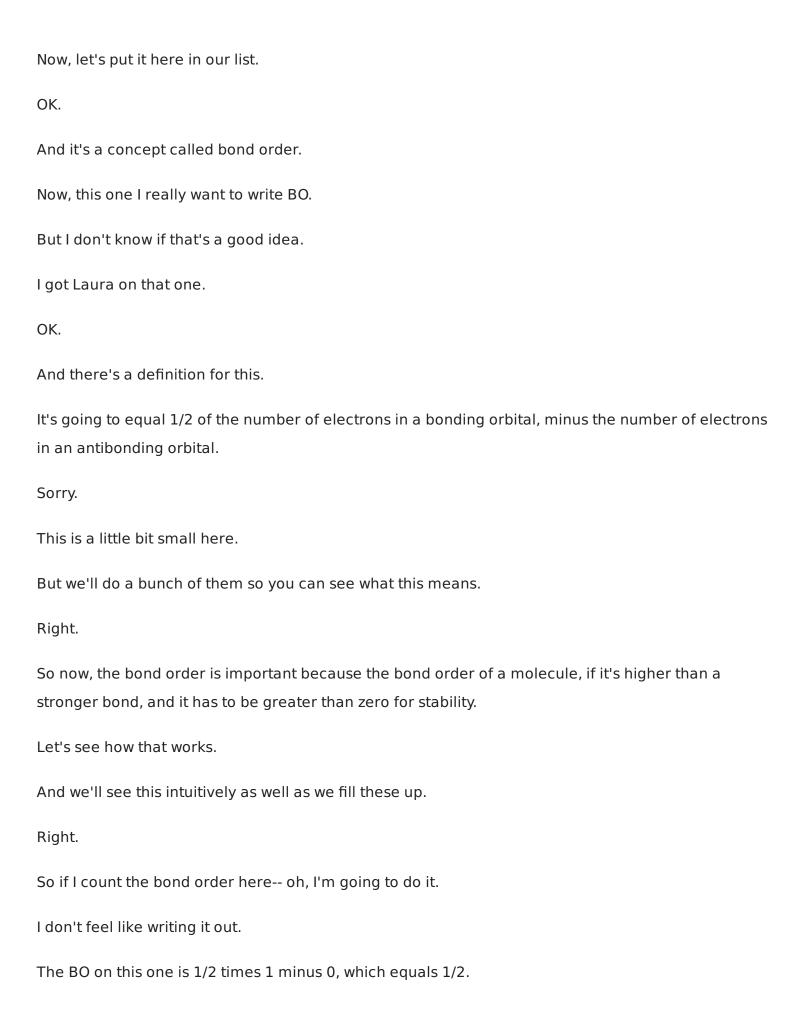
And the way we refer to the antibonding orbital is with a little star.
They're both sigma because they both satisfy that.
Right.
They're both sigma cause they both have symmetry around the inter nuclear bonding axis.
But now, see, OK.
So that's good.
But now let's fill them.
Let's fill them.
Because 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.

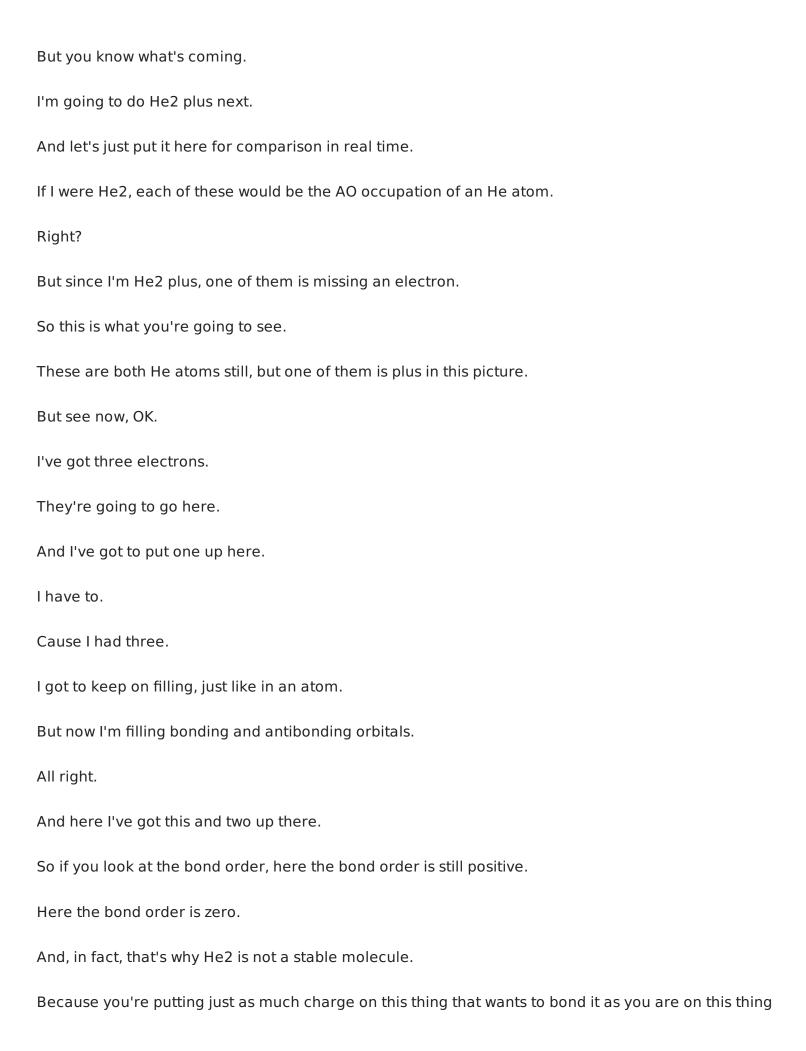


OK.
These are my MOs, sigma, sigma star, 1s, 1s.
Oh, boy.
So if that's H and that's H plus, and they're coming together to make H2 plus that's what's in the middle there.
That's the molecule.
All right.
Well, then I also can now fill in the starting AOs.
So let's do that.
That's it.
Because somebody 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.

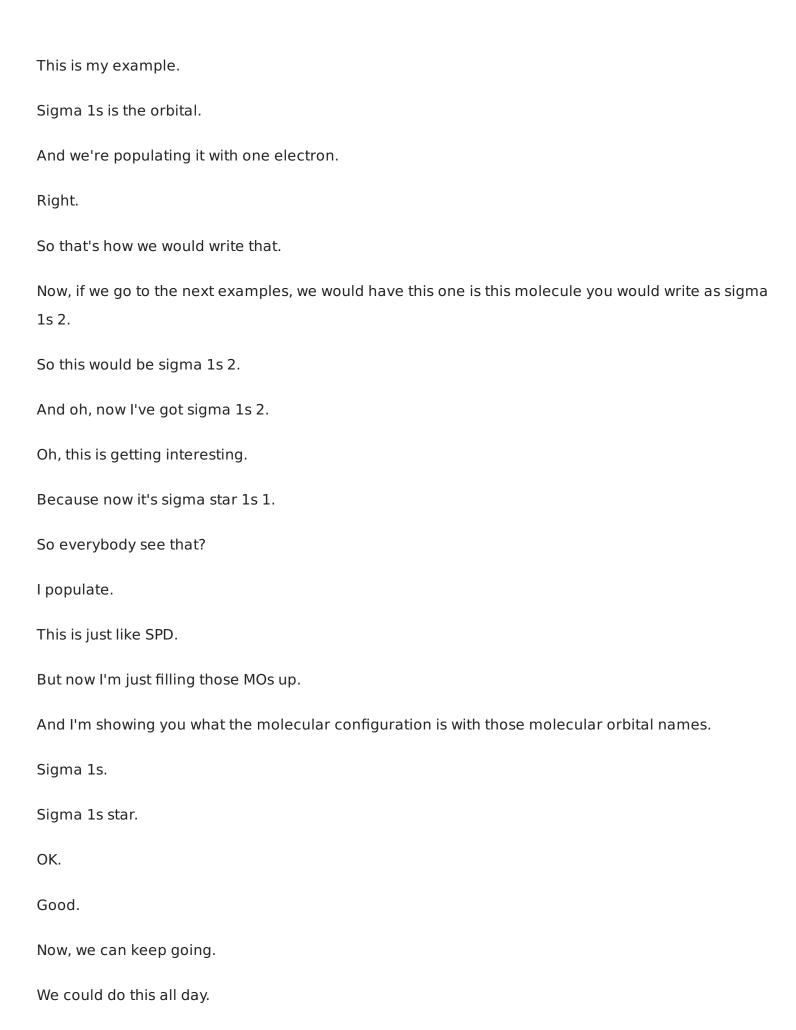
And that is a very important concept.

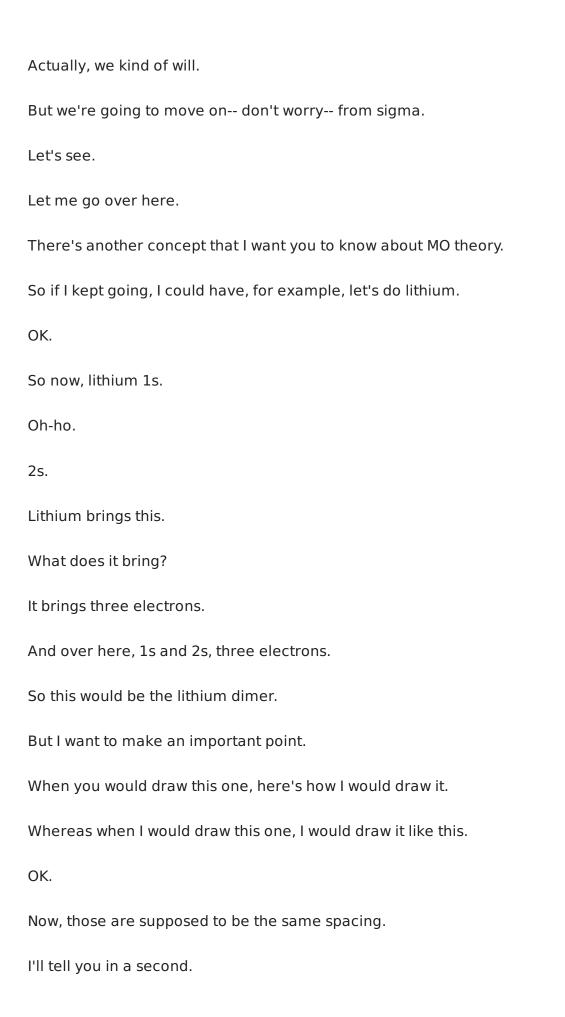


OK.
Good.
It's 1/2.
Well, it's greater than 0.
So right away I know that the H2 plus molecule is probably stable.
That's good.
But let's go to some more examples now.
Let's do a few more.
All right.
Now we're going to work our way to H2.
And in this case, energy is always going up in these diagrams.
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 H2.
Now, the bond order here is equal to 1.
Right?
I didn't have any electrons in an antibonding orbital.
All right.



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 He2.
But He2 plus has a bond order that's similar.
Did I get something wrong?
He2 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 H2 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]





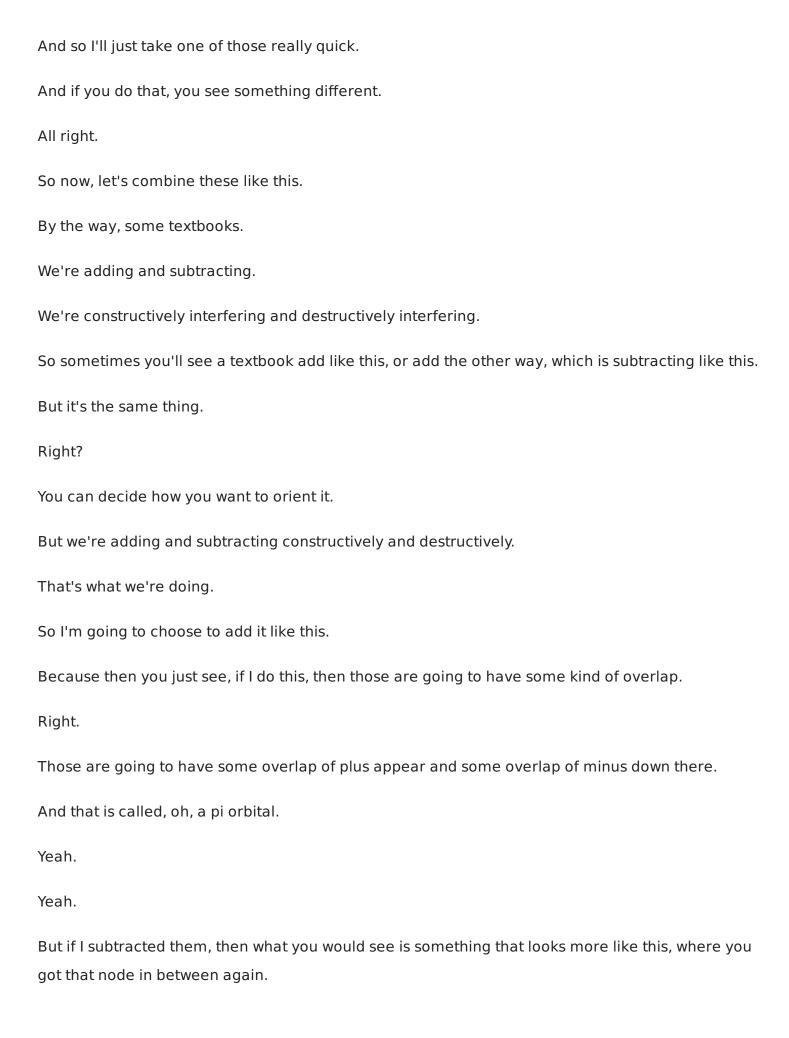
Notice that the distance here between the bonding and antibonding orbital is larger than it is here.
The reason is because it's related to the overlap.
So there's another point, which is that the overlap of AOs is related.
So the greater the overlap of AOs, the greater the change in energy between bonding 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.
Γhese sigma 1ses oh, sigma 1s.
What do you think these are called?
2s.
Sigma 2s.
Sigma 2s.
Siama 2s.



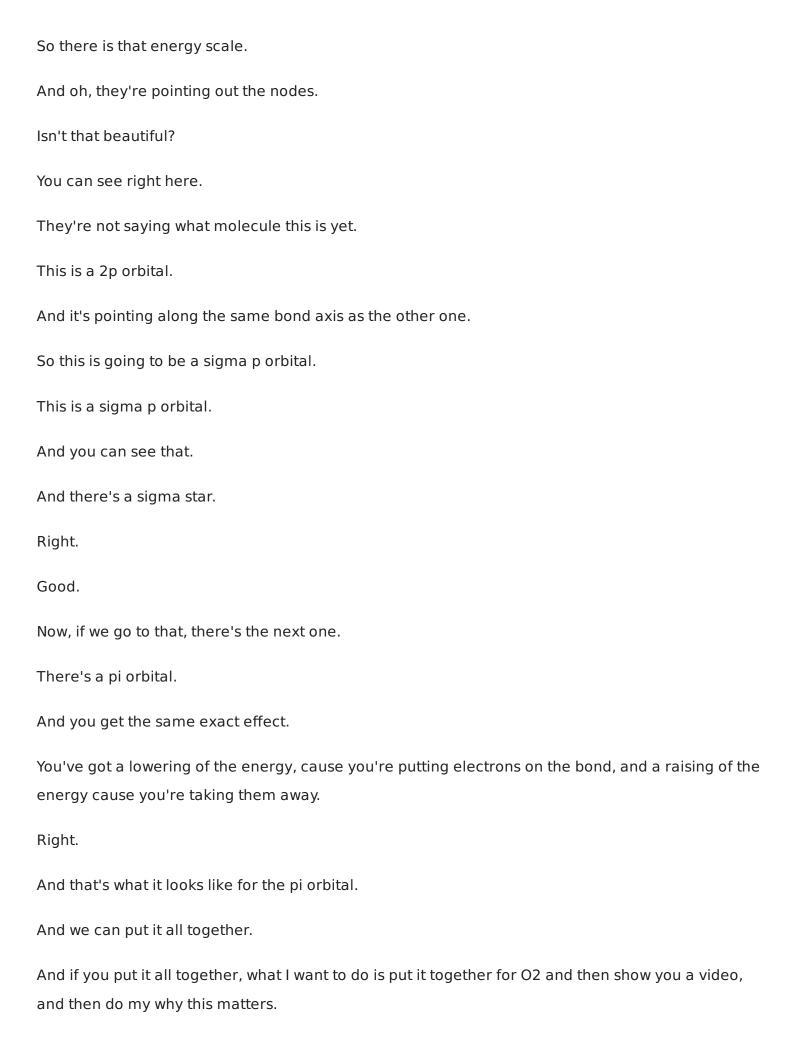
What else do you have this is what you do on a Friday.
After I watch Dr. Quantum I'm going to just add every single one of these with every single one.
It's finite.
It's not going to take forever.
Let's just do p.
OK.
Now, with p orbitals there's something interesting that happens, because now that sign 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 pz as the one along the axis.
Remember, there's px, py, and pz.
When we solve for the p orbitals, those are the Ms. Those are the Ms. Right.
One.

Zero.
And minus 1.
Now, by convention we put the pz 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 pz 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 px oh, well, let's actually subtract these.
OK.
So minus, plus, minus.
Now, what you see is something very different, right.

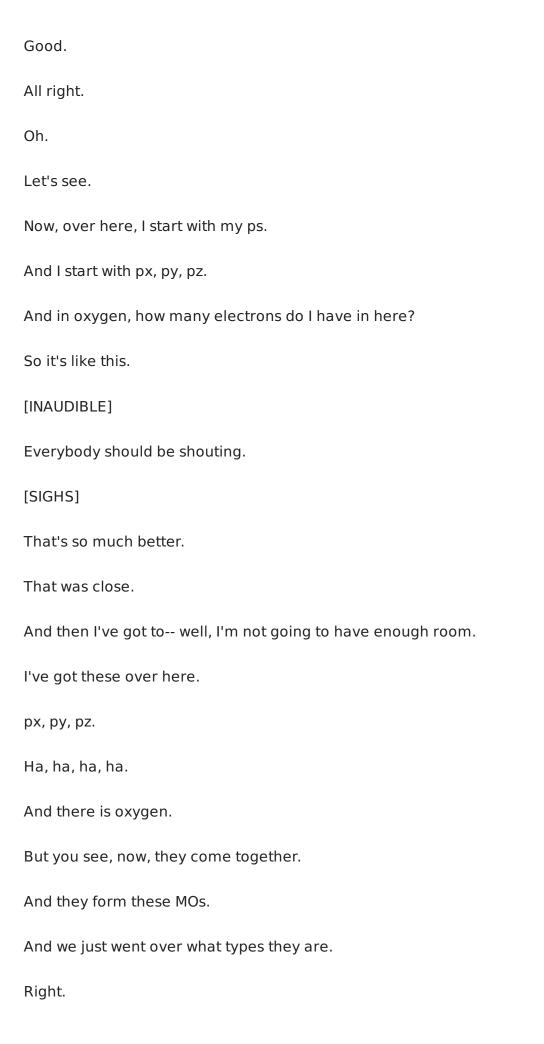
So now, oh, boy.
Can I draw this?
Maybe.
I don't know.
OK.
I'll take that.
Right.
And so now what you see so I'm subtracting these.
And so the density goes down.
And now, you're going to get minus, minus.
Right.
Plus, plus.
But I've reduced the electron density.
And even worse, I'm back to that situation 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.



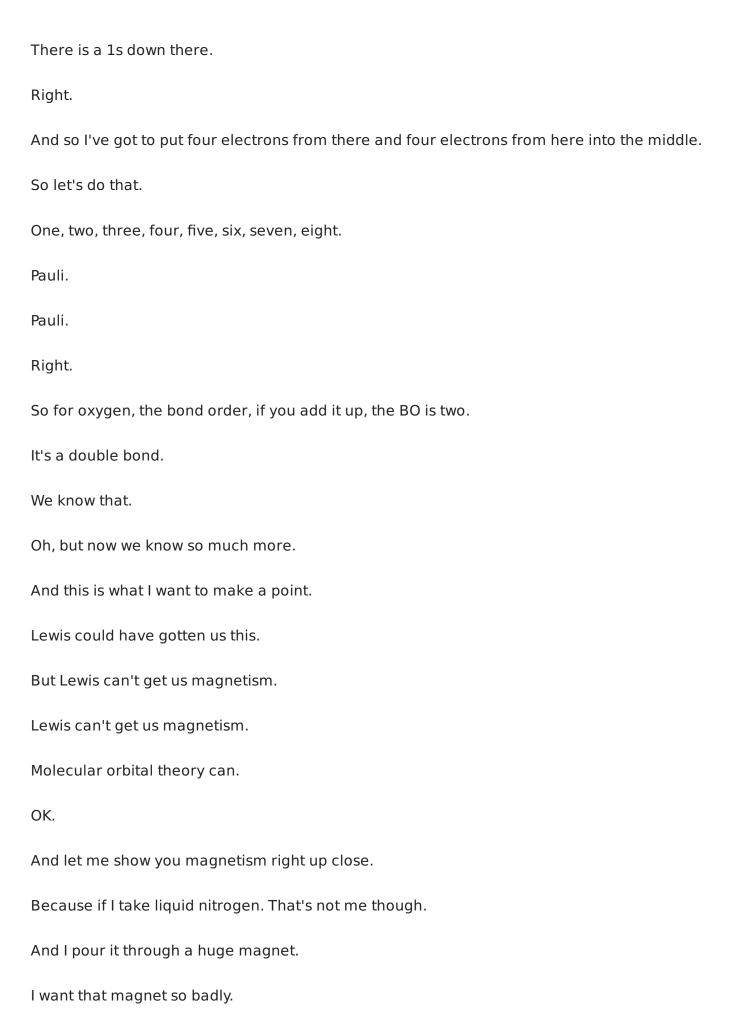
Right.
And this would be a pi star orbital.
This would be for like px orbitals.
Now, notice, these cannot be sigmas, because the pi orbital is not symmetric around the bonding axis.
OK.
These cannot be sigmas.
But that's why we have another symbol for them.
Luckily, we've got a lot of symbols, and the 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.

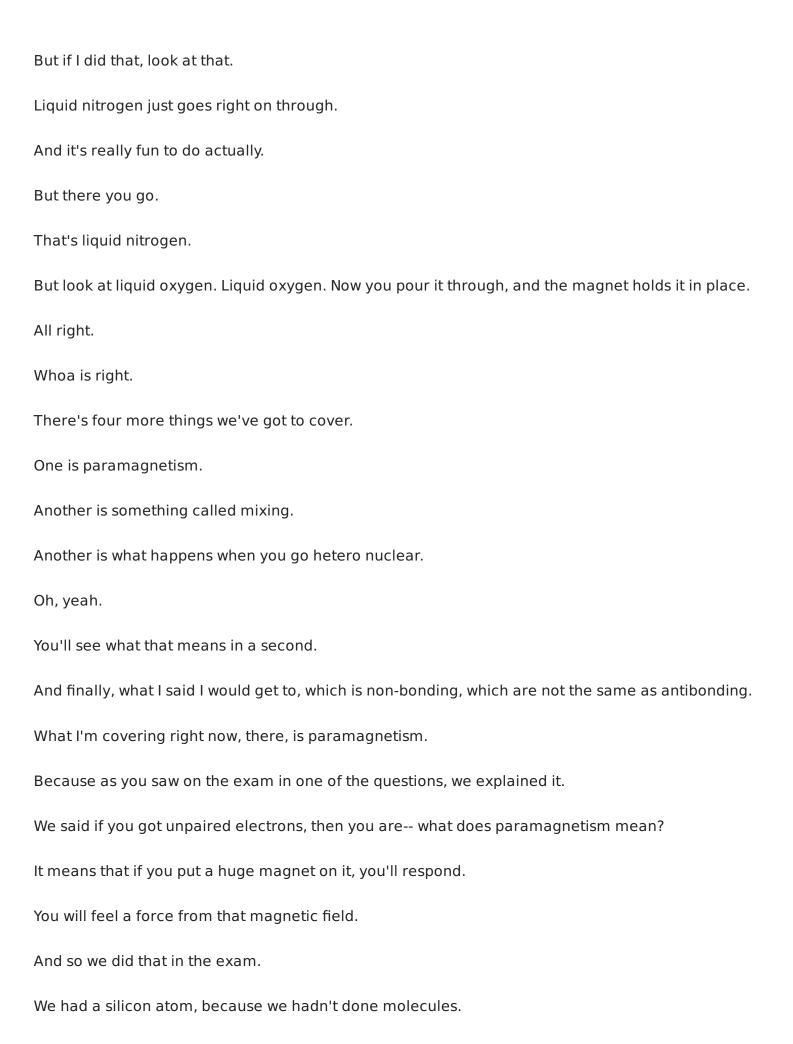


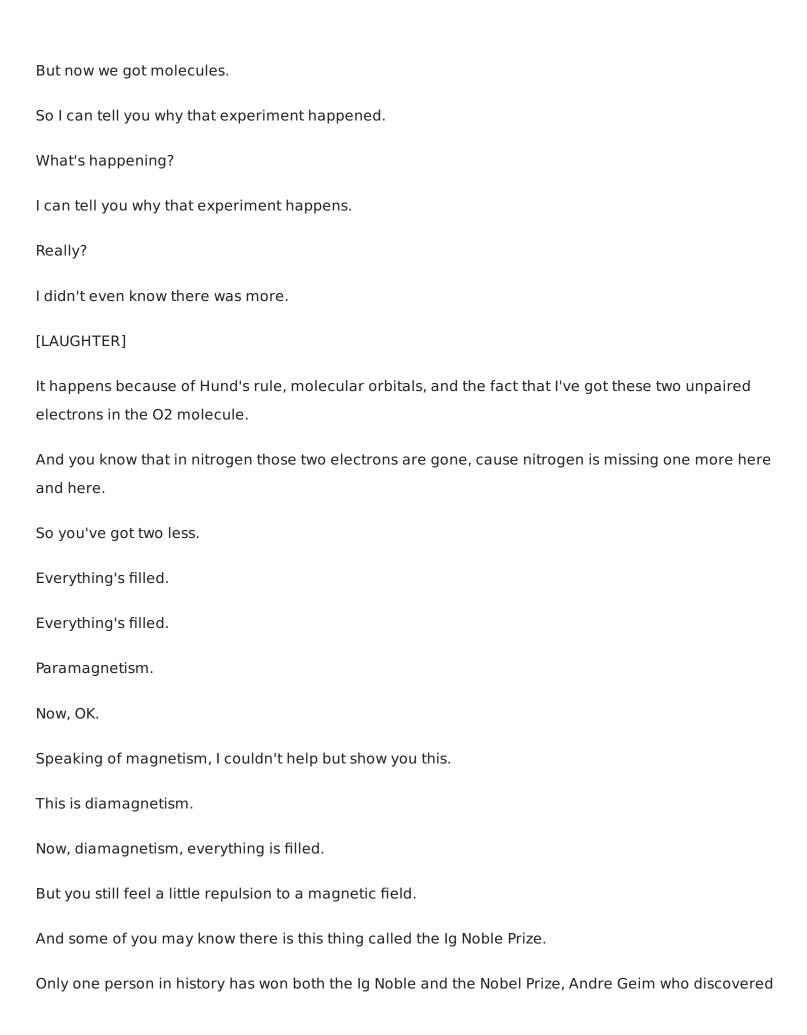
Now, if you put this together, I'm going to show you the system for oxygen and nitrogen. OK.
And then we'll do a couple other cases too.
But we're going to do oxygen first.
So if I take oxygen, then I'm not even going to write 1s anymore.
That's way down in energy.
It's not really involved in the bonding.
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.



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.



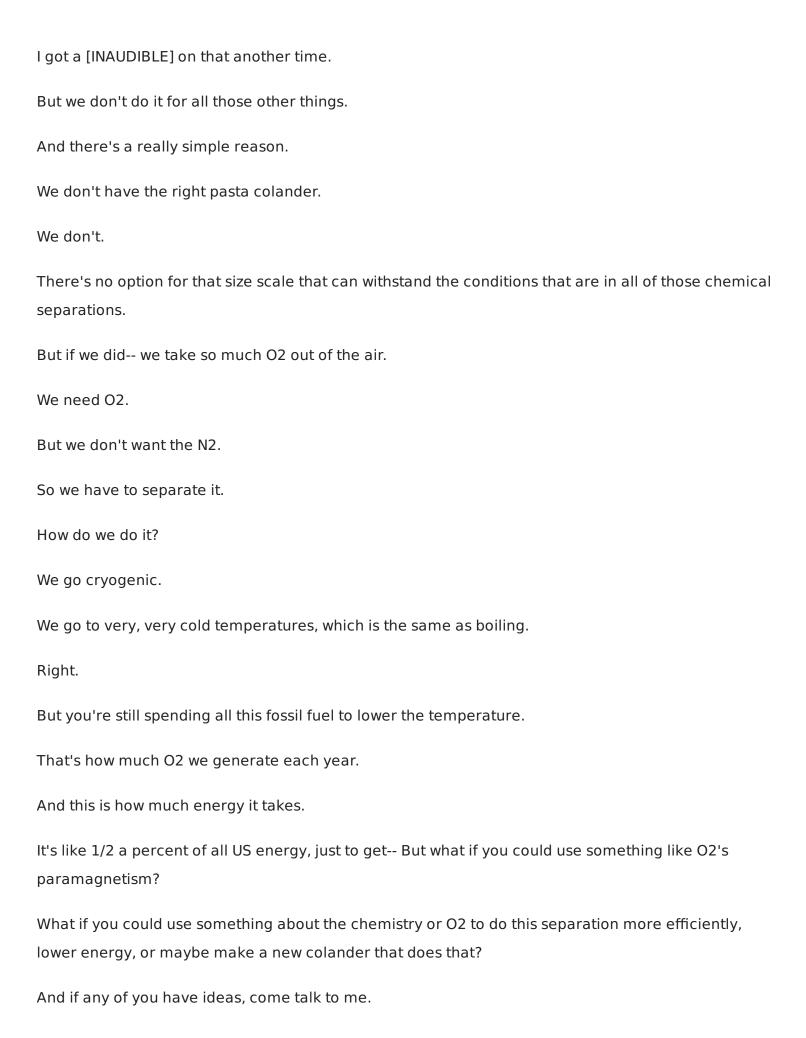




graphene with scotch tape.
But before that he won the Ig Noble Prize because he did this to frogs.
Because water is diamagnetic.
And so it repels a magnetic field.
It's just got to be really, really high.
I hope that frog was OK.
It looked sort of OK.
So the frog was floating.
And it was like a study 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 O2, 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.



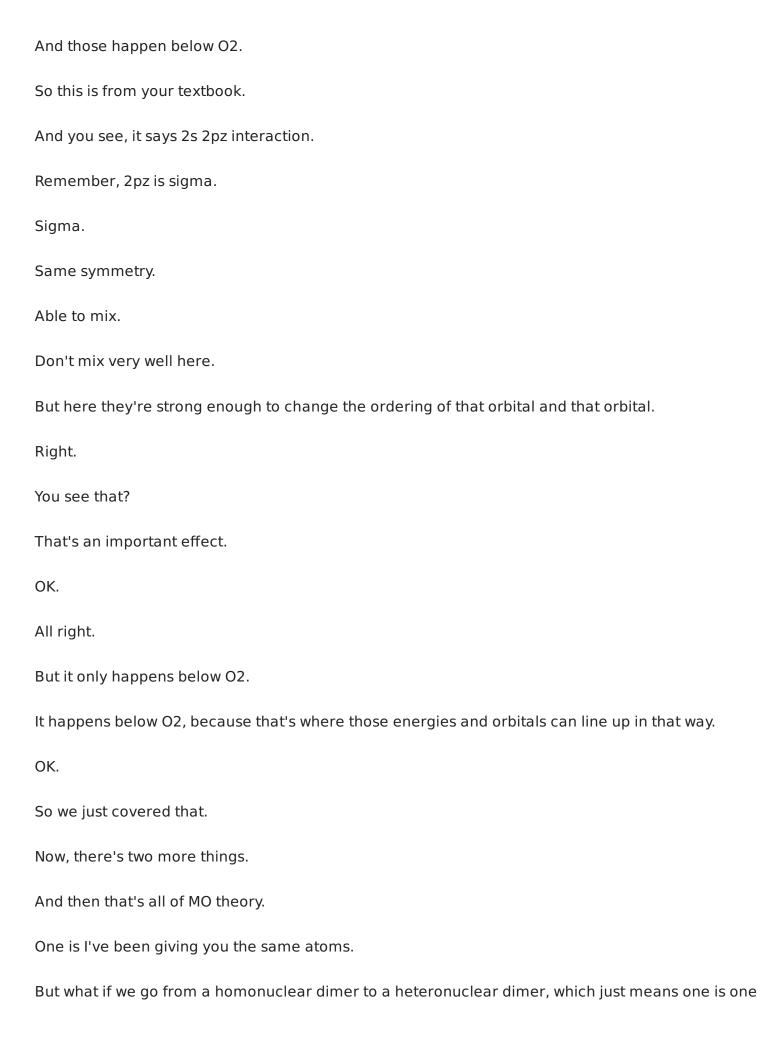
It goes on and on.
And it will go all the way down the Infinite Corridor.
And this is how we do chemistry.
In fact, has anyone seen this on the side of the road?
That's a distillation column.
It's a big pasta cooker.
That's all you're doing is boiling one molecule off of another over a long time with 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.



This is a problem I care a lot about.
OK.
Ah.
But I had some other paramagnetism.
Unpaired electrons.
We got that one.
На.
[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 N2, 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 N2, because they are still all filled. But it is important. Because if I were to pull an electron out of N2, it would come from a sigma orbital, not a pi orbital, because of those interactions.



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

But CI 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

and one is another type of atom.

In the meantime, have a very good weekend.

cases.