## Introduction

We've discussed Lewis structures and the VSEPR model of bonding. Both of these are **models** - that is, they just show how atoms tend to bond. What they don't do is provide a theoretical explanation for **why** the molecules are put together that way. As scientists, we'd like to be able to have a theory that can give an explanation for why atoms bond as they do. We'd also like to use the theory to predict observable properties other than structure!

There are many theories that explain bonding - some simple, some complex. None are perfect. As beginning chemists, we'd prefer a simple theory that we can use to explain most things we'd encounter in the lab. The simplest useful theory of bonding is called **valence bond theory**, and we will briefly discuss it. Valence bond theory is not perfect, and fails to completely describe quite a few molecules, but it is good enough for us at this point.

## Valence bond theory: what is it?

What **is** valence bond theory? From the name, we know that this theory involves the valence electrons of an atom - that is, the electrons in the atom's outermost **atomic orbitals**. Valence bond theory has this to say about how bonds are formed:

1. Bonds are formed when two atoms are close enough together so that their **orbitals overlap**. In other words, electrons from both atoms may be in a region of space which is claimed (or **shared**, if you prefer) by both atoms. Remember that we defined covalent bonding as electron sharing.
2. Each set of two overlapping atomic orbitals can contain at most a total of two electrons. Orbitals containing one electron each can overlap and bond. Orbitals that already contain two electrons can only bond with empty orbitals. A bond between a full orbital and an empty one is called a **coordinate covalent bond**.

What do these two statements mean? From the first, we get the notion that molecular geometry must be dictated by the overlapping orbitals. From the second, we can see why the smaller noble gases almost never bond. Where would an atom like **neon** put any electrons? All its orbitals contain two electrons. You can verify that by writing out the electron configuration.

## A picture of valence bonding

We'll now look at valence bonding graphically. This should help you visualize the points we just made above. We start with the simplest case possible - the hydrogen atom.

Hydrogen has only one electron, and it's in an "s" orbital. (Hydrogen's electron configuration would be written $1s^1$.) So, hydrogen would bond with another element when its half-full 1s orbital overlapped with another half-full orbital from another atom. For simplicity, let's look at hydrogen bonding with another hydrogen to form the $H_2$

molecule.

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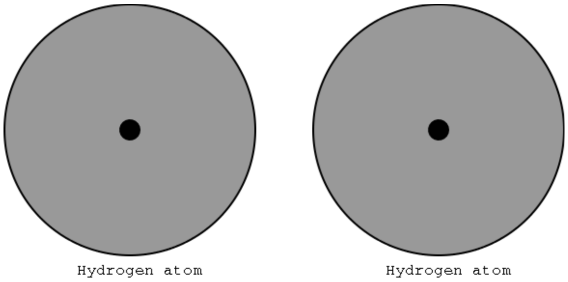
|  | • The dark gray areas represent the 1s orbital of the hydrogen atom.<br>• The black dot represents the nucleus of the hydrogen atom (not to scale).<br>• Each hydrogen has one electron in this orbital. |
| Illustration 1: Two hydrogen atoms | |

To bond, these two hydrogen atoms must come together so that their 1s orbitals **overlap** and form a bond.

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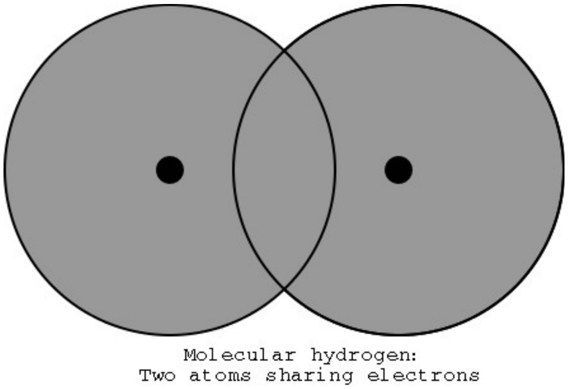
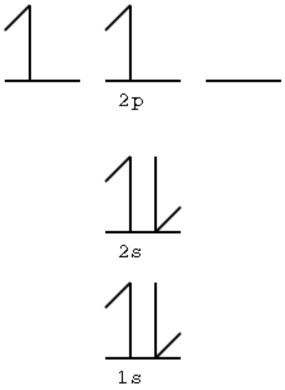
|  | • The area of overlap between the two hydrogen atoms is the bond.<br>• Since the area is part of **both** hydrogen atoms, the electrons are **shared** between the atoms - forming a covalent bond.<br>• The bond is located between the atoms and touches an imaginary line drawn between the bonded atoms. This type of bond is called a sigma ( $\sigma$ ) bond. |
| Illustration 2: The $H_2$ molecule | |

This picture agrees with the Lewis dot formula for hydrogen. The Lewis formula has one unpaired electron, suggesting that it will form one bond (which it does). That unpaired electron represents the unfilled "s" orbital.

## Hybridization

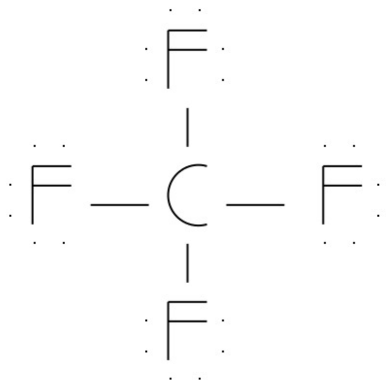
Let's look at a more complex atom like carbon. Carbon is an important element for life, and it has been extensively studied. Carbon's electron configuration is $1s^2\mathbf{2s^2 2p^2}$. Carbon has **four** valence electrons, and if you drew a Lewis formula for carbon, it would have four unpaired electrons. This suggests that it is capable of forming four bonds. In the Lewis structures you've drawn so far, you've seen carbon form four bonds.

Valence bond theory predicts that bonds will be made with half-filled orbitals. If we draw an orbital diagram for carbon, we can see that carbon has two half-filled orbitals and one empty orbital. So how can it form four bonds?

|  | • The 1s orbital is filled. It's not in the valence (outer) shell, and it does not participate in bonding.<br>• The 2s orbital is filled.<br>• Two of the 2p orbitals are half-filled and one is empty.<br>• We need **four electrons** to completely fill all the orbitals here. |
|---|---|
| Illustration 3 - Orbital diagram for the carbon atom | |

This is where the notion of **hybridization** comes in. Hybridization is the combination of atomic orbitals to make new ones that describe the bonding in the molecule. Orbitals themselves are mathematical functions - probability distributions of electrons in an atom. These can be combined with other orbitals mathematically. We're not going to go into the math, but we will describe in qualitative terms how these combinations work.

Let's say we're dealing with carbon in a carbon tetrafluoride molecule: $CF_4$. If we were to describe this molecule, we would say that it is a tetrahedral molecule with carbon at the center. Its Lewis structure would look like this:

|  | • There are four bonds around the carbon.<br>• This compound is tetrahedral.<br>• This compound is nonpolar due to symmetry. |
|---|---|
| Illustration 4 - Lewis structure of $CF_4$ | |

How can we make our valence bond theory agree with this? We allow the valence orbitals to combine and form new orbitals which can bond to form the compound. When we combine orbitals:

1. The **number of electrons** on the atom **does not change**.
2. The **overall number of orbitals** does **not** change. (the **type** does change, though)

For carbon to bond four times, it needs four unfilled orbitals. In addition, the orbitals need to be identical except for the direction they point in - since all four carbon-fluorine bonds in $CF_4$ have been verified by experiment to be identical. If we combine the three 2p and one 2s orbital into a set of four identical orbitals (which we will call "$sp^3$ hybrid orbitals"), we can form four identical bonds with four fluorine atoms. Our new orbital diagram will look like this:

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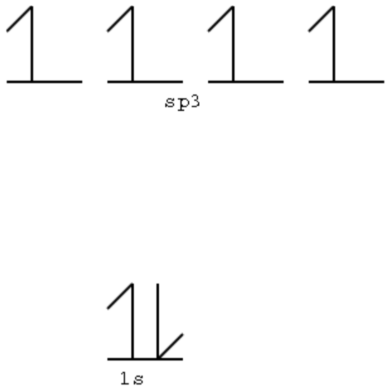
|  | • We now have four half-filled identical orbitals, much like the Lewis formula for carbon indicates.<br>• We still have four valence orbitals and four valence electrons - same as we started with.<br>• The 1s orbital is unchanged (it's not involved in bonding).<br>• If there had been a **lone pair** of electrons on this atom, it would have appeared in the orbital diagram as a **filled orbital**. You can see an example of this in the orbital diagram of nitrogen in the $NH_3$ molecule.<br>• The energy of each $sp^3$ hybrid orbital formed here is less than the energy of a 2p orbital but greater than the energy of a 2s orbital. |
| Illustration 5 - An orbital diagram showing the $sp^3$ hybrid orbitals of carbon in $CF_4$ | |

In graphical form, these hybrid orbitals would look like this:

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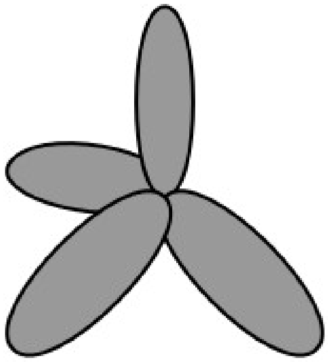
|  | • The orbitals form the shape of a tetrahedron.<br>• Each orbital contains one electron (it is half filled).<br>• The carbon nucleus is at the center - hidden from view in this illustration.<br>• Each of the four orbitals overlaps with orbitals from a fluorine atom (not shown), forming sigma ( $\sigma$ ) bonds. |
| Illustration 6 - A graphical representation of the $sp^3$ hybrid orbitals of carbon in $CF_4$ | |

Different kinds of hybrid orbitals are formed depending on the geometry of the molecule (including lone pairs - lone pairs are just **filled** orbitals!). Here's a list of the types of hybrid orbital compared to the shape of the molecule.

| ***Type of hybrid orbital*** | ***Number of orbitals used*** | ***Shape of molecule*** |
|---|---|---|
| sp | 2 | linear |
| $sp^2$ | 3 | trigonal planar *or* bent with one lone pair |
| $sp^3$ | 4 | tetrahedral, (trigonal) pyramidal, *or* bent with two lone pairs |
| $sp^3d$ | 5 | trigonal bipyramidal (and its derivatives) |
| $sp^3d^2$ | 6 | octahedral (and its derivatives) |

Sometimes "d" orbitals form hybrids and bond. Atoms that violate the octet rule generally bond this way. The hybrid orbitals formed include some empty "d" orbitals. Examples of this are $PCl_5$ and $XeOF_4$. Try drawing Lewis structures for these molecules.

Single bonds and double bonds and triple bonds, oh my!

So far, we've only talked about single bonds. We'd like to apply valence bond theory to double and triple bonds as well. According to valence bond theory, bonds are formed by orbital overlap between atoms. Single bonds are formed by overlap **on the axis between the atoms** by hybrid orbitals. Double and triple bonds are formed **by a different kind of overlap**.

First, we'll look at a double bond. Valence bond theory explains **any** bond as an overlap of orbitals on the bonding atoms. So a double bond involves the overlap of **two** sets of orbitals (two orbitals from each bonding atom). How does this explain the difference in energy? Let's look at the valence bond picture of the bonding in ethylene - $C_2H_4$.

Ethylene has this Lewis structure:

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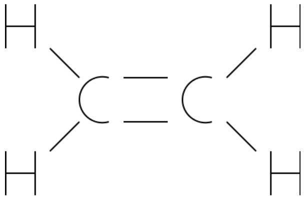
|  | • The structure contains a carbon-carbon double bond at the center.<br>• The geometry around each carbon is **trigonal planar**. |
| Illustration 7 - Lewis structure of $C_2H_4$ | |

We would expect that the carbon atoms in this structure would have **sp$^2$** hybrid orbitals. Carbon's orbital diagram then looks like this:

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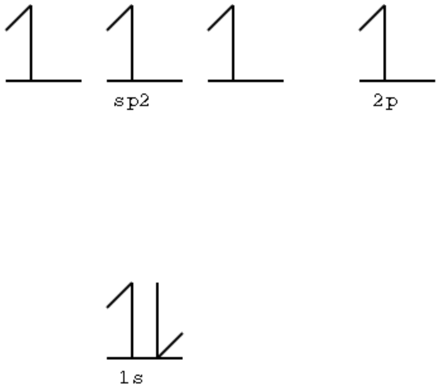
|  | • Three hybrid orbitals are formed.<br>• One of the 2p orbitals is left unchanged.<br>• The sp$^2$ hybrid orbitals have slightly less energy than the 2p orbital, but the energies are close enough so that the 2p orbital gets an electron before electrons begin to pair in the sp$^2$ orbitals.<br>• As before, the 1s orbital is unchanged, and does not participate in the bonding. |
| Illustration 8 - An orbital diagram of carbon in $C_2H_4$ showing sp$^2$ hybrid orbitals | |

We can represent this graphically. The three sp$^2$ hybrid orbitals on the carbon will be arranged in a trigonal planar geometry. The half-filled p orbital will also be present.

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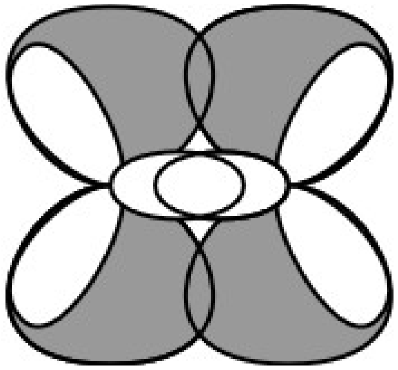
|  | • The p orbitals are shown in gray. Two p orbitals - one on each atom - are shown.<br>• The sp$^2$ hybrid orbitals are shown in white. Six sp$^2$ orbitals - three on each atom - are shown. They are drawn slightly smaller so that we can see the p orbitals.<br>• The carbon nuclei are located at the centers where three sp$^2$ orbitals meet. |
| Illustration 9 - Bonding orbitals in $C_2H_4$ | |

If we look at the picture of the double bond that valence bond theory provides, we can see that there are two different kinds of bonds making up the double bond in ethylene, We define the two types of bond like this:

1. *Sigma* ( $\sigma$ ) *bonds*: These bonds are formed when orbitals overlap **along a line drawn between the nuclei** of the two bonding atoms. You get this situation when "s" orbitals overlap (as in $H_2$). You also get this situation when hybrid orbitals overlap, since hybrid orbitals always point along the lines between the bonded atoms. Sigma bonds tend to have **good overlap** between the bonding orbitals, so sigma bonds are

**strong**. They're hard to break apart. **Single bonds are always sigma bonds, and double and triple bonds have one sigma bond each**.

2. *Pi ( π ) bonds*: These bonds are formed when orbitals that aren't pointed at each other overlap. Pi bonds are normally formed when **off-axis** "p" orbitals overlap (as in $C_2H_4$). As you can tell from the picture, the overlap in a pi bond isn't as good as the overlap in a sigma bond, so pi bonds tend to be **weaker** than sigma bonds. In other words, it's often easier to break apart a pi bond than a sigma bond.

What about triple bonds? How does valence bond theory describe the triple bond? The Lewis structure of $C_2H_2$ (commonly called acetylene) contains a triple bond.

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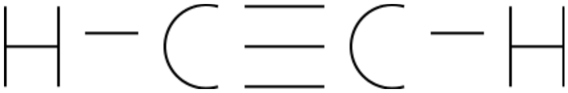
|  | • The structure of this molecule is linear around each of the carbon atoms.<br>• There are only two things surrounding each carbon, so they move as far apart as possible. |
| Illustration 10 - Lewis structure of $C_2H_2$ showing a triple bond. | |

The geometry around the carbon atoms is linear. According to valence bond theory, that would mean each carbon has **sp hybrid orbitals** (see the chart in this note pack). The orbital diagram for a carbon atom in the $C_2H_2$ molecule would look like this:

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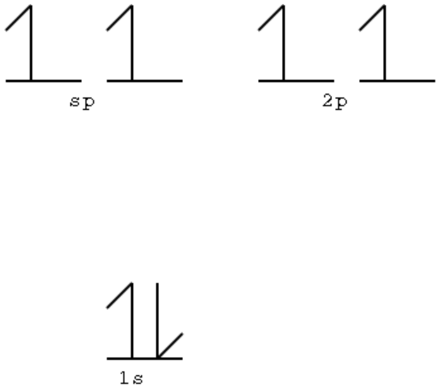
|  | • As always, we started with four valence orbitals and ended up with four valence orbitals.<br>• Two sp hybrid orbitals were formed, while two "p" orbitals were unchanged.<br>• The 1s orbital is not involved in bonding. |
| Illustration 11 - An orbital diagram showing the sp hybrid orbitals of carbon in $C_2H_2$ | |

Without some 3D plotting software, the picture would look too cluttered on this page – so we'll visualize it in our minds. Think about how the carbons in $C_2H_2$ are bonded. How do the sp hybrid orbitals bond? One of the sp hybrid orbitals bonds with the hydrogen. This is a sigma bond. The other sp orbital bonds with an sp orbital on the other carbon - another sigma bond. That leaves the p orbitals. As in the case of the double bond, the p orbitals form pi bonds. This time, we have two pi bonds. These are practically identical except for the direction the p orbitals face. One set points up-and-down and the other set points in-and-out.

For practice, describe the bonding of the carbon atom in carbon dioxide ($CO_2$) using valence bond theory. (*Hint: Draw the Lewis structure first, find the shape of the molecule, and* ***then*** *describe the bonding!)*

Double bonds and rotation: Support for the valence bond theory

In a compound containing only single bonds, atoms are able to rotate about each other without a chemical reaction. In molecules like ethane ($C_2H_6$) and 1,2-dichloroethane ($C_2H_4Cl_2$), these rotations require little energy and happen rapidly.

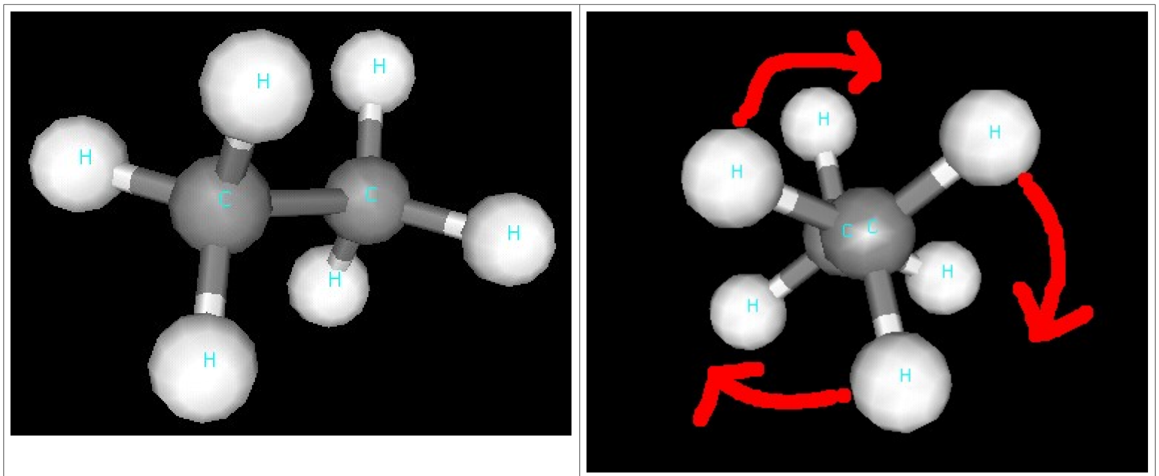


Illustration 12 - Two views of $C_2H_6$

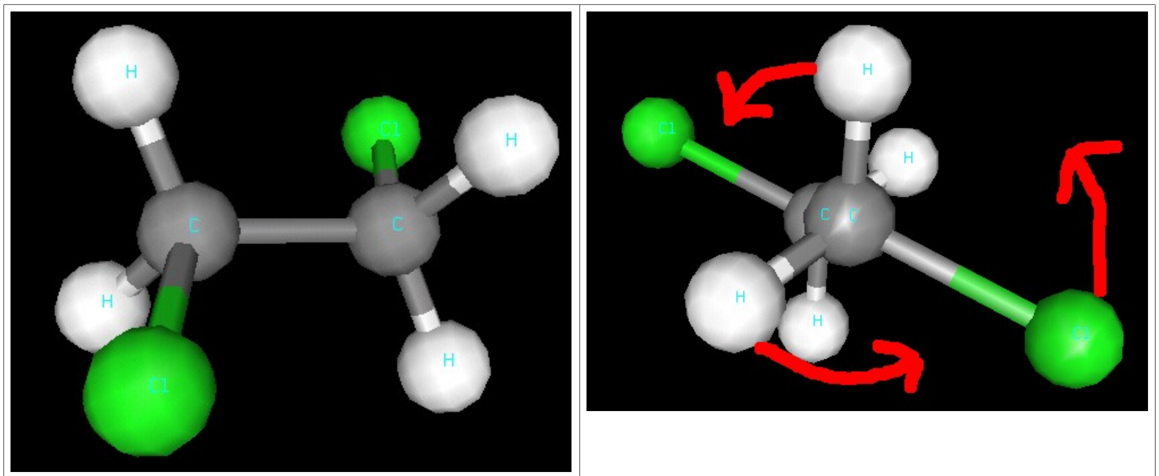


Illustration 13 - Two views of $C_2H_4Cl_2$

Rotation in both of these molecules is about the carbon-carbon single bond in the center.

Now consider 1,2-dichloroeth**ene** ($C_2H_2Cl_2$). There are actually two distinctly different molecules with that name (unlike 1,2-dichoroethane, which represents only a single kind of molecule. They are called **isomers**, since they have the same chemical formula but a different arrangement of atoms.

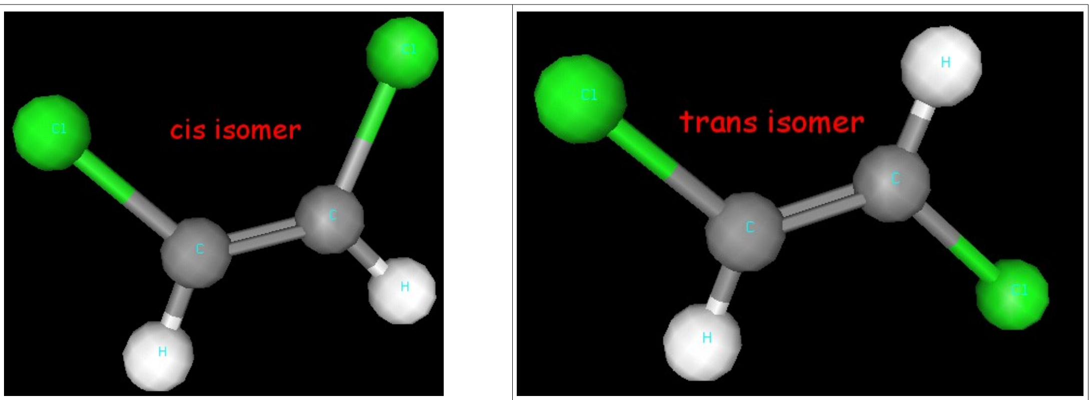


Illustration 14 - *cis* and *trans* 1,2-dichoroethene

The *cis* form has both chlorine atoms on the same side of the double bond, while the *trans* form has chlorine atoms on opposite sides of the double bond.

These isomers have different physical and chemical properties (polarity being one important difference). The fact that they can exist at all as separate molecules is easy to explain using the valence bond idea of how a double bond forms. The single bond can rotate without changing the overlap of the orbitals that make up the bond, since that overlap is on the axis between the bonded atoms. This is true for the sigma part of the double bond, too. The **pi** part, on the other hand, is an **off-axis** overlap. Rotating around the axis between the carbons in, say, cis 1,2-dichloroethylene would require breaking at least the pi part of the double bond. This requires **substantially** more energy than rotating around the single bond in the 1,2-dichloroethene. In other words, the rotation around a double bond requires a **chemical reaction**.

## Summary

This note pack contains most of the information you need to know about valence bond theory for this course. We have described the basic postulates of valence bonding, and have shown how we can use the theory to explain the existence of a few simple isomers. We've also linked the type of bonding in a molecule to the shape of the molecule, and we've discussed the concept of **hybrid orbitals** to explain how certain species (like carbon) can form up to four bonds.