

Chapter 28

SHAPE, Part 1

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Now, let's get into shape.

The shape of a polyatomic unit is very important. It is, after all, a big part of identity; we first introduced this way back in Chapter 2.

“ EVERY MOLECULE IS IDENTIFIED BY A SPECIFIC NUMBER OF SPECIFIC ATOMS IN A SPECIFIC ARRANGEMENT.

Notice that there are three parts to a molecule's identity. "Specific number" is how many. "Specific atoms" refers to which elements. "Specific arrangement" includes shape such as plane, pyramid, diamond, etc. It also means which atoms are at what corners of the plane, pyramid, diamond, etc. ALL THREE PARTS TOGETHER DEFINE AND IDENTIFY THE CHEMICAL UNIT. All three together give rise to all the properties of that unit. IF YOU CHANGE ANY ONE OF THE THREE PARTS, THEN YOU CHANGE THE IDENTITY AND YOU HAVE A DIFFERENT CHEMICAL UNIT WITH A DIFFERENT SET OF PROPERTIES. This is extremely important.

Water is water. A water molecule is composed of one atom of oxygen and two atoms of hydrogen. The oxygen atom is in the middle and the hydrogen atoms are bonded to it at an angle. That's water's chemical unit. Every water molecule is that way. Every molecule of that type is identified as water. ”

Notice that, even back in Chapter 2, we had touched upon the importance of shape to physical and chemical properties. There are so many things that depend on shape, including your own life. Let me give you a simple illustration using water. As noted in the description from Chapter 2, the hydrogens of the water molecule are bonded to the oxygen, bent at some angle and not in a line. Now, let's fast-forward to Chapter 10: to a considerable extent, the weirdness and the magic of water results from the polarity of the molecule. Here's the catch: if the hydrogens of the water molecule were bonded in a line instead of bent at an angle, then water could not be polar. Life could not exist as we know it. The surface of Earth could not exist as we know it. All because of the wrong shape.

Polarity is a very important property of any compound, not just water. Polarity has a massive influence on physical and chemical properties. Polarity has an important role when dealing with phases and solutions, as we shall see beginning in Chapter 37. Polarity can also have a big effect on how things react. We shall see the connection between polarity and shape by the time we get through all of this in Chapter 29. Even without polarity, shape itself still has a strong effect on chemical reactivity. The reason is quite simple: some shapes are more prone to react than others.

At this time, we embark on a journey of diversity: the diversity of shape. Although there are many different shapes possible, there is a systematic approach for determining the shape of many polyatomic units. This is where we go now. The system is called VSEPR. It's not perfect, but it's very good.

28.1 VSEPR

VSEPR is the acronym for the Valence Shell Electron Pair Repulsion system of determining shape. Although the acronym is spelled V-S-E-P-R, we pronounce this as "*vesper*".

"Valence Shell Electron Pair Repulsion" is certainly a mouthful but the term is easy to break down. The system is based on Repulsions between the Electron Pairs in the polyatomic unit. But not just any electron pairs; specifically, we look at the electron pairs from the Valence Shell of the atoms involved. Just how do we know about the valence shell electron pairs? That's easy: they're the ones in the Lewis structure. They're the lone pairs and the bond pairs. The VSEPR system begins with the information from the Lewis structure.

When we say "shape", we refer to the specific, 3D arrangement of two or more atoms bonded to a central atom. Lone pairs are a big part of all repulsions to consider and lone pairs do influence shape, but lone pairs are not included in the term "shape". SHAPE relates only to ATOM POSITIONS. By the way, VSEPR determines the shape around central atoms only. There is no such thing as doing the shape of a terminal atom since it is bonded to one other atom only, by definition.

In VSEPR, the big R is the big key: Repulsion. Spin exclusion between electrons of the same spin and electrostatic repulsion between negative electrons are the big factors here. The grand result is that orbitals of bond pairs and lone pairs on the central atom want to be at maximum separation from each

other. This orientation will give the least repulsion overall. It is this orientation of least repulsion that is so critically important in VSEPR, as we shall see. This is what leads to shape.

Although we deal with repulsions due to bonding electrons, the overall shape is not affected by bond order. For example, in BeF_2 , there are two single bonds but, in CO_2 , there are two double bonds. In both cases, the central atom is bonded to two other atoms. Both molecules are the same shape (linear) and the bond orders don't matter. It's really the number of bond connections which counts, regardless of the orders. The number of bond connections is the same as the number of atoms which are bonded to the central atom; thus, you can simply count these and avoid confusion by bond orders.

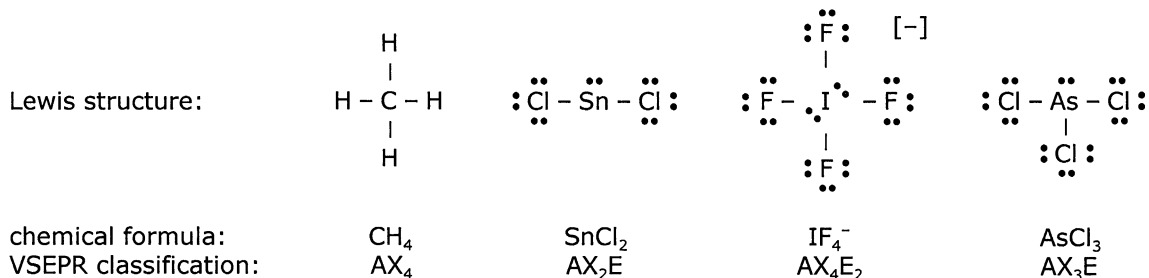
VSEPR's disregard for bond order comes in handy when doing polyatomics which have delocalization. As noted in the last Chapter, the primary emphasis for resonance structures lies in the bonds, and those variations involve bond orders. Since VSEPR does not care about bond order, then VSEPR does not care about resonance. You determine the shape for any resonance structure and that will be your answer for all resonance structures. (There is a twist to this for cases of resonance between two or more central atoms. These aren't common at this level and I won't cover them, although your instructor might.) Here's another benefit: since VSEPR doesn't care about resonance, then we only need the six Basic Steps for doing Lewis structures here. There is no reason to optimize formal charge for doing VSEPR.

At this time, I want to introduce a new, generic formulation which is very often used in VSEPR. This new formulation looks like a chemical formula but it's a VSEPR classification. The generic format is AX_nE_m . (Some people use different symbols, such as AB_nE_m , but they mean the same thing.) Every central atom in every polyatomic unit can be classified according to this format. Here's what you need to know.

- The AX_n part indicates n number of any atoms X bonded to A.
This is similar to AX_n as used in Chapter 26 but now it's more general: the X's can be any atoms (same or different elements) and they can be terminal atoms or other central atoms.
- The E represents lone pairs on atom A; there is m number of these lone pairs.
- All E's are relative to atom A only; lone pairs on X's don't count for A and are not included in m .
- All X's and all E's and the numerical values of n and m are determined from the Lewis structure.

➤ ➤ ➤ THAT'S THE CONNECTION TO LEWIS!

Let me show you how this works with a few examples. Here are some of the Lewis structures from Chapters 26, now with their VSEPR classification.



I'll pick SnCl_2 to run through in detail as follows:

Sn is the central atom.

Sn has two atoms attached to it, so $n = 2$.

Sn has one lone pair on it, so $m = 1$.

With $n = 2$ and $m = 1$, the classification is AX_2E . (You don't have to show subscripts of 1.)

You should go through the other examples and be certain that you can see how the VSEPR classification is derived in each case. Note that the AX_nE_m designations are generic and can be applied to neutral molecules or to ions; they are not chemical formulas, and they need not include charges for ions.

Alright, let's head into things a bit more. First, one final note. We are doing shape. We are dealing with three dimensions. I will present diagrams for this, but diagrams are 2D and they don't always give a clear picture for 3D. The best way for you to learn this is to get a model kit. There are kits available for making models of molecules, and these are the best way to really get to understand this shape business. You may be able to purchase one or borrow one from someone. (It's very possible that you

will need a model kit for later chem classes anyway, if you are going on, but check with your instructor about that.) Not all model kits will cover all examples we do here, but that's OK; work with whatever you can get. In lieu of model kits, computer animation works pretty well. Although this is a 2D image again, there are good programs and even free websites for this. Your instructor may have recommendations for these. Check them out sometime.

This ends the preliminaries. Now it's time for your orientation.

28.2 How repulsive!

We must return to the notion of the orientation of least repulsion. This is a lengthy term, so I will abbreviate it as OLR. Let me point out that these "orientations of least repulsion" go by different names in different sources and with different instructors. It doesn't matter. Use any term you want to use or need to use for your class. The important thing is that you remember that these represent a maximum separation between all the repulsive components, which gives the least overall repulsive effects.

Each repulsive component in this picture is either a lone pair or a bond connection (of any bond order). The OLR gives the directions of these in three dimensions around the central atom. Ultimately, all VSEPR shapes are derived from these orientations. There are five orientations which we shall consider. For any central atom in any polyatomic unit, its orientation of least repulsion is determined by the sum of the number of lone pairs plus the number of bonded atoms. THIS IS VERY IMPORTANT. I'll say it once more for emphasis.

THE OLR FOR ANY CENTRAL ATOM IS DETERMINED BY THE SUM OF THE NUMBER OF LONE PAIRS PLUS THE NUMBER OF BONDED ATOMS.

You can determine this all-important sum from the Lewis structure. I'll demonstrate this for the Lewis structures which were shown above.

- CH₄ Carbon is central. It has zero LPs and four bonded atoms. The sum is four. There are four repulsive components to accommodate around the carbon atom.
- SnCl₂ Tin is central. It has one LP and two bonded atoms. The sum is three. There are three repulsive components to accommodate around the tin atom.
- IF₄⁻ Iodine is central. It has two LPs and four bonded atoms. The sum is six. There are six repulsive components to accommodate around the iodine atom.
- AsCl₃ Arsenic is central. It has one LP and three bonded atoms. The sum is four. There are four repulsive components to accommodate around the arsenic atom.

You can also find this sum from the VSEPR classification: it's just $n + m$. Let's repeat the same examples.

CH ₄	AX ₄	$n + m = 4 + 0 = 4$	There are four components to accommodate.
SnCl ₂	AX ₂ E	$n + m = 2 + 1 = 3$	There are three components to accommodate.
IF ₄ ⁻	AX ₄ E ₂	$n + m = 4 + 2 = 6$	There are six components to accommodate.
AsCl ₃	AX ₃ E	$n + m = 3 + 1 = 4$	There are four components to accommodate.

This method is real handy and this is one of the reasons that the AX_nE_m classification is used.

For the five orientations which we cover, the sums will run from two through six. Let's now start into what these orientations really look like.

- SUM = 2

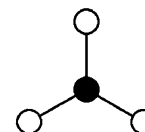
For a sum of two, the orientation of least repulsion occurs when the two repulsive components (open circles) are completely opposite each other around the central atom (dark circle) as shown at right. Everything in this orientation is on a straight line and this orientation is called "linear". Geometrically, we refer to the two positions as lying at 180° relative to each other around the center. (Angles will be important as we go, so keep them in mind.)



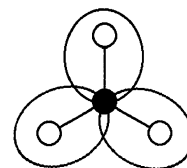
- SUM = 3



For a sum of three, the orientation of least repulsion is obtained when the three components point toward the corners of an equilateral triangle. Everything is in the same plane and this gives the term "trigonal planar". Trigonal means three-sided; sometimes "triangular planar" is used. The three repulsions lie at 120° from each other, which is the same as the central angle of an equilateral triangle.



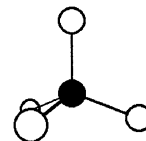
Now, right away, I want to point out something. I'm drawing these figures as ball-and-stick pictures. These drawings are common for shapes because they are clear. Sticks are good for showing bond connections (of any order), but they hide the underlying repulsions between the orbitals which are involved. Take a look at the drawing at right; this picture is meant to convey the sense of orbitals for the trigonal planar case. In reality, the orbital fields are quite sizeable and this is how the repulsions arise. The more of these repulsions which you cram around one central atom, the more drastic are the repulsions overall. Every additional repulsion gets more and more crowded. This is what's really behind VSEPR.



- SUM = 4



For a sum of four, the orientation of least repulsion is called "tetrahedral". A "tetrahedron" is a special kind of pyramid: it has all equal faces, it has all equal edges, and it has all equal angles. For a central atom with tetrahedral OLR, the atom is at the center of the pyramid and each of the four components is aimed at a corner of the tetrahedron. The angles between the four components are 109.5° . (That's after rounding. If you're picky, it's $2 \cos^{-1}(3^{-1/2})$ or $109.4712206\dots^\circ$, but who's picky?)



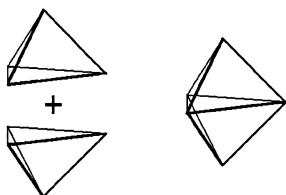
Beginning with tetrahedral, we are now into three dimensional objects. It will be harder to understand these from a 2D picture. This is where model kits get to be even more important.

Before I go to the next OLR, I need to make a point about the first three.

For linear orientation, the two objects around the center will point in different directions but they are otherwise identical. We say the two positions are equivalent. For trigonal planar orientation, the three objects around the center are also identical in all aspects except for direction. These are also equivalent. For tetrahedral orientation, all four positions are equivalent, although this may not be as obvious; if we picture a tetrahedron as a pyramid, we tend to think that the base and sides of a pyramid can be different, but that is not true for a tetrahedron. Every face is the same, so any face can be the base; it doesn't matter. The result is that the four points of a tetrahedron are equivalent.

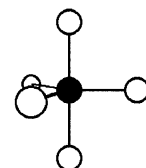
Let's go on to the other two OLRs.

- SUM = 5

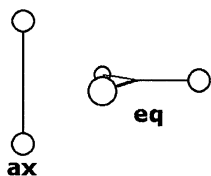


For a sum of five, the orientation of least repulsion is a bit tricky. The orientation is called trigonal bipyramidal, although we usually just say tbp. Let me first describe a trigonal bipyramid. As you can guess, it's based on a pyramid, but "bi" means there are two of them. Trigonal again means three-sided. Thus, a "trigonal bipyramid" is composed of two trigonal (three-sided) pyramids. This is shown at left. You can also think of a tbp as a five-pointed diamond.

The five points of the tbp represent the orientation of least repulsion around the central atom, which would lie at the very center. This orientation is shown at right.



Now, we have some peculiarities. The five points of the tbp are NOT all equivalent. The five points can be divided into two sets, and these two sets are called axial and equatorial; these two sets are broken apart at the left. (The central atom is not a part of either set, so it is excluded from the diagram at left.)



To help remember the terms axial and equatorial, consider a globe for planet Earth. The Earth spins on its axis, the North and South Poles. The corresponding points of the tbp are the very top and very bottom points: these two are called axial points or axial positions. Earth has an equator; likewise, the tbp has an equator which is defined by the other three points; these three are called equatorial points or equatorial positions. We typically abbreviate axial as "ax" and equatorial as "eq". The axial points represent a linear pair; as such, each ax point is located 180° from the other. The equatorial points make up a trigonal plane (which is shown in the diagrams as nearly on edge); as such, each eq point is located 120° from each other. The axial points are on a line which is perpendicular to the center of the equatorial plane. This gives us a 90° angle between any one equatorial point and any one axial point.

Let me summarize these geometric peculiarities of tbp. The tbp orientation is composed of two types of positions. There is an equatorial set of three points; all of these are equivalent to each other in the set. There is an axial set of two points; both of these are equivalent to each other. But an equatorial point and an axial point are not equivalent to each other. This will be very important later. With respect to angles, there are three angles involved in tbp orientation.

90° (any eq to any ax)

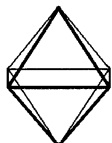
120° (eq to eq)

180° (ax to ax)

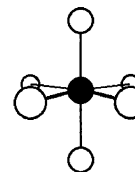
Out of all five of our orientations of least repulsion, tbp is the trickiest. Be careful with this one. You may need to go over this several times in order to get comfortable with it.

Let's go on to our final OLR.

- SUM = 6



For a sum of six around a central atom, the orientation of least repulsion is called "octahedral". Although the prefix "octa-" refers to its eight faces, we are interested in its six points; we can think of this as a six-pointed diamond. All faces of the octahedron are equal, all edges are equal and all six points are equal. For a central atom with octahedral orientation, the six repulsive components are in the direction of the six points and these are all equivalent. There's another way of viewing the octahedral orientation: imagine the central atom at the origin of an xyz coordinate system. The six components lie along the axes in both + and - directions. Each point is 90° to four neighbors and 180° to the point opposite.



Since everything is equal in the octahedron, this is much simpler than the tbp case. Take careful note, however! Because both tbp and octahedral can be considered as diamonds, many students think the octahedral orientation also has equatorial and axial differences, just like tbp. That's wrong. All six points in the octahedral orientation are equivalent; there are no equatorial and axial distinctions for the octahedron in VSEPR.

This concludes our five orientations of least repulsions. Time to summarize. Circle the list below and the five sentences below that. They're all very important. You may need to come back here.

SUM ($n + m$)	ORIENTATION OF LEAST REPULSION	ANGLES
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°
5	trigonal bipyramidal	90°, 120°, 180°
6	octahedral	90°, 180°

All shapes which we shall cover are derived from these five orientations. Keep in mind that "shape" goes only by atom positions; lone pairs are not included in the term "shape". There are two consequences of this.

- If a central atom does not have lone pairs, then its shape and its OLR are the same.
- If the central atom has one or more lone pairs, then the shape and its OLR will be different.

We'll see these things as we go through a large number of examples.

Let me make one more point about those angles. They're not just idle inclusion in this material. Shape gives us the overall layout of the polyatomic unit. Beyond that, we can go into two more details with respect to the exact structure of the unit. One of those details is bond length, which tells us how long the bond connections are. We discussed bond length in Chapter 25, so that detail has already been covered. The other detail is bond angle, which is the angle defined by two atoms around a central atom. Let me illustrate using BeF_2 , mentioned earlier: the angle defined by the positions F-Be-F is 180°. That's the bond angle. The angles for the OLRs, as given above, are the starting points for evaluating bond angles by VSEPR. The actual bond angles in actual compounds may be different from those but the above angles still provide a starting point. We shall see later why those differences arise. But that's later. For now, we consider overall shape.

28.3 What shape are we in?

Now we turn to the steps for doing the shape of a polyatomic unit by VSEPR.

- **Step 1.** Start with the Lewis structure of the polyatomic unit. Alternatively, you can start with the AX_nE_m classification, if that is provided information.

If you are only given a chemical formula, then you must do the Lewis structure in order to start into VSEPR. If you are given a specific AX_nE_m designation, then you can just do VSEPR from there.

- **Step 2.** Find the sum of the number of bonded atoms and the number of lone pairs on the central atom.

This is the ever-important $n + m$ sum. From the Lewis structure, you count the number of bonded atoms plus the number of lone pairs. It's that easy. From the AX_nE_m formula, you simply add $n + m$. It's that easy.

- **Step 3.** Choose the orientation of least repulsion for the given sum.

That's in the part which you circled on the prior page.

- **Step 4.** Enter the atom positions into the orientation and determine the correct shape.

In this step, you base the shape only on atom positions.

By the way, if the polyatomic unit has more than one central atom, then you do the VSEPR steps for each central atom separately, one at a time. I mention this now, but we won't do an example of this type until we run through everything in Chapter 29. All of our examples at first will have only one central atom.

We'll now start into a number of Examples here and into the next Chapter. In fact, there are thirteen variations on shape, so we're going through thirteen Examples. I'll work with specific molecules and polyatomic ions and I'll be relating these to the AX_nE_m format as we go.

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Example 1. BeH_2 . That's as simple as it gets.

.....
 ▶ Step 1. You need a Lewis structure. There's not much to it.



▶ Step 2. The central atom (Be) has two atoms attached to it and it has zero lone pairs. This gives a sum of two. In VSEPR format, this is AX_2 .

▶ Step 3. For a sum of two, the orientation of least repulsion is linear. The angle of the orientation is 180° .



▶ Step 4. The hydrogen atoms are entered at both positions of the OLR. The resulting shape is also linear. The H-Be-H bond angle is 180° .

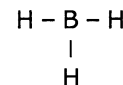


Notice that the shape is the same as the OLR; this is because there are no lone pairs on the central atom.

There was not much to this example. They won't all be this easy. I guarantee it.

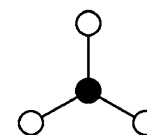
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Example 2. BH_3 .

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 ▶ Step 1. Lewis structure.

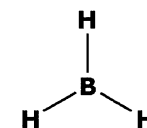


▶ Step 2. The boron has three atoms attached to it and it has zero lone pairs. This gives a sum of three. This corresponds to the VSEPR classification AX_3 .

▶ Step 3. For a sum of three, the orientation of least repulsion is trigonal planar. The angles are 120° .



▶ Step 4. The hydrogen atoms are located at all three of the trigonal planar positions. This gives the shape as trigonal planar. All H-B-H bond angles are 120° .

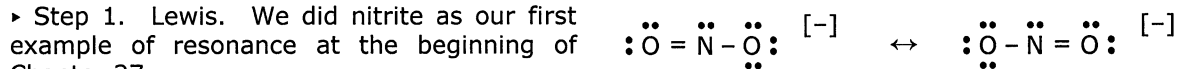


Done.

Both examples so far had no lone pairs on the central atom; for all such cases, the shape is the same as the OLR. Now, we'll see what happens with lone pairs on the central atom.

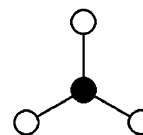
Example 3. Nitrite ion.

► Step 1. Lewis. We did nitrite as our first example of resonance at the beginning of Chapter 27.

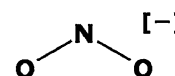


► Step 2. Pick either resonance structure; it doesn't matter which. The central N has two atoms bonded to it and it has one LP. The sum is three. The VSEPR classification is AX₂E.

► Step 3. The orientation of least repulsion is again trigonal planar.



► Step 4. The terminal atoms are located at two of the trigonal planar positions. (All three positions are equivalent, so it doesn't matter which two get the terminal atoms.) The LP on the central nitrogen atom occupies the third trigonal planar position, but the LP does not count toward shape. The resulting shape is shown at right; this is simply called "bent" shape.



Whenever the central atom has one or more lone pairs, then the shape will differ from the OLR. Lone pairs influence shape by being a part of the OLR but the term for shape goes only by atom positions. This distinction is critical to the VSEPR system.

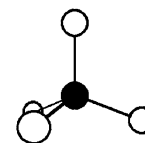
By the way, NO₂⁻ has the same VSEPR classification, AX₂E, as SnCl₂ which was mentioned earlier in this Chapter. The nice thing about VSEPR classification is that EVERY COMPOUND WITH THE SAME VSEPR CLASSIFICATION HAS THE SAME SHAPE. Thus, SnCl₂ is also of bent shape.

Example 4. Silicon tetrachloride.

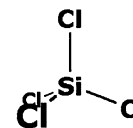
► Step 1. Lewis structure: you do it.

► Step 2. Since you're doing the Lewis structure, I'll just tell you that its classification is AX₄. There are four bonded atoms and zero lone pairs on the central atom. The sum is four.

► Step 3. For a sum of four, the orientation of least repulsion is tetrahedral. All angles are 109.5°.



► Step 4. The chlorine atoms are located at all four tetrahedral locations. This gives the shape as tetrahedral. All Cl-Si-Cl bond angles are 109.5°.

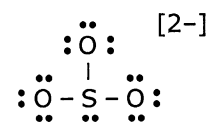


Notice again that there are no lone pairs on the central atom, which means that the shape is again the same as the OLR.

Like SiCl₄, CH₄ is also AX₄ as previously noted in this Chapter. Since EVERY COMPOUND WITH THE SAME VSEPR CLASSIFICATION HAS THE SAME SHAPE, then CH₄ is also tetrahedral and its bond angles are also 109.5°.

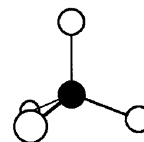
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Example 5. Sulfite ion. This was one of the first polyatomic ions mentioned way back in Chapter 3 and I drew its shape back then. Now, we will derive that shape.

► Step 1. Lewis structure.

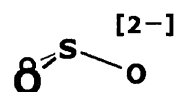


► Step 2. The sulfur atom has three atoms attached to it and it has one LP. The sum is four. The VSEPR classification is AX₃E.

► Step 3. The orientation of least repulsion is tetrahedral.



► Step 4. The oxygen atoms occupy three of the tetrahedral positions. Since all positions are equivalent, it does not matter which three. The fourth position is a lone pair, but this does not apply to shape. Ignoring the LP, we have another pyramid with a three-sided base. This shape is called "trigonal pyramidal". When you make this one with a model kit, one thing that sticks out is that it is a very squatty pyramid. But we don't say "very squatty pyramid" for shape.

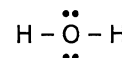


What compound did we talk about in this Chapter that was also AX₃E? _____

What shape is that ion? _____

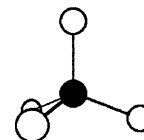
.....
Example 6. Water. As noted way back in Chapter 2, water molecules are bent. Now we'll see how that is derived.

► Step 1. Lewis structure.

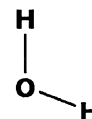


► Step 2. Oxygen has two atoms attached to it and it has two LPs. The sum is four. The VSEPR classification is AX₂E₂.

► Step 3. The orientation of least repulsion is tetrahedral.



► Step 4. The hydrogen atoms occupy two tetrahedral positions; since all tetrahedral positions are equivalent, it does not matter which two. The other two positions are lone pairs. Taking into account only the atom positions, the shape is described as "bent".



That's it.

This is our second example with bent shape, but the two cases arise from two different OLRs. In this case and for any other AX₂E₂, the shape is bent and the angles are based on the 109.5° angles of a tetrahedron. Our prior bent example was NO₂⁻: for any AX₂E, the shape is bent but the angles are based on the 120° angles of a trigonal plane. Do the angles matter? Yes, they can.

We have completed six of the thirteen variations on shape. This would make for a convenient place to break. Our next shapes are based on tbp and these are tricky, just like tbp itself. If you're OK for now, then press on. Otherwise, you might want to go back over the ones here first.

Problems

1. What is the orientation of least repulsion and shape for each of the following classifications?
 - a. AX_2E
 - b. AX_3E
 - c. AX_3
 - d. AX_2E_2
 - e. AX_4
 - f. AX_2
2. What is the shape for each of the following?
 - a. PF_3
 - b. CO_2
 - c. NO_3^-
 - d. O_3
 - e. NF_4^+
 - f. $SeCl_2$