

1 SHAPES OF MOLECULES: VSEPR MODEL

1.1 INTRODUCTION

- The shapes of molecules tend to be controlled by the number of electrons in the valence shell of the central atom. The *valence-shell electron-pair repulsion* (VSEPR) model provides a simple method for predicting the shapes of such species.
- The Cambridge Structural Database contains a wealth of diverse molecular geometries, and provides the ability to visualise and manipulate molecules in three-dimensions. This is vitally important in order to study and understand the shapes adopted by particular molecules.

1.2 OBJECTIVES

- To investigate shapes of molecules by analysing experimental crystal structure data.
- To understand the factors that determine the preferred shape adopted by particular molecules.
- To use the valence-shell electron-pair repulsion (VSEPR) model to predict the shapes of given molecules.

1.3 GETTING STARTED

- Open the interactive WebCSD teaching database by going to the following URL:

http://webcsd.ccdc.cam.ac.uk/teaching_database_demo.php

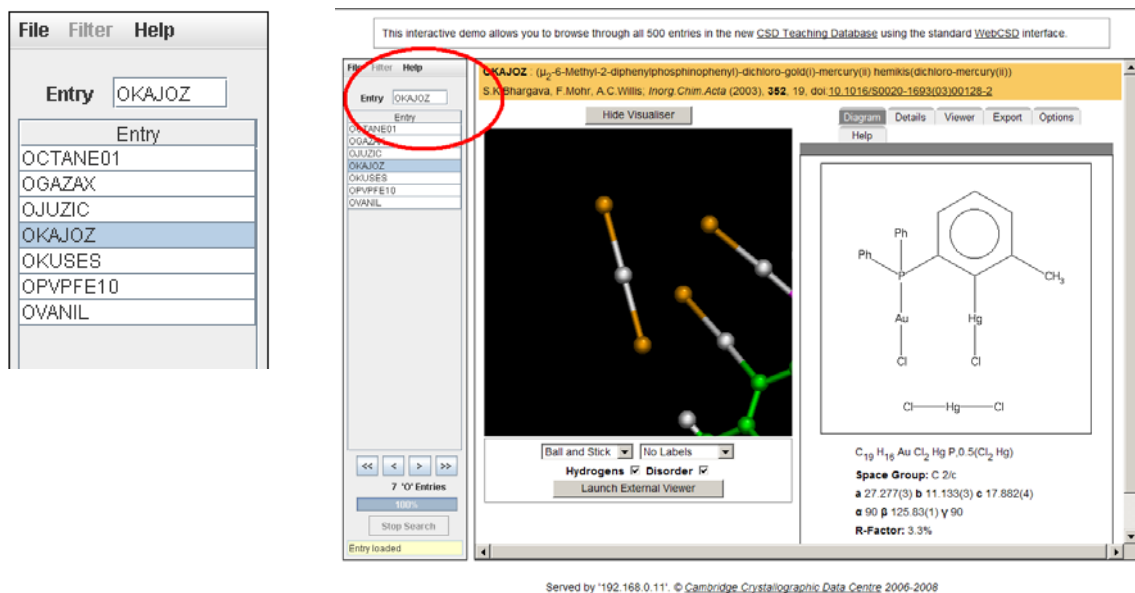
- This demo version of WebCSD allows you to browse all 500 entries in the teaching subset of the Cambridge Structural Database.
- Reference codes (refcodes) of the structures in the teaching set will appear in a list on the left hand side of the WebCSD page. Only those refocde beginning with “A” are displayed intially. To show those refcodes starting with “B” click on the > button.
- To view a structure select the corresponding refcode in the list by left-clicking on it. Alternatively, you can type a refocde in the **Entry** box above the structure list.

1.4 STEPS REQUIRED

1.4.1 Examine the structures of di-, tri-, and tetrachloro mercury

- Consider the following series of molecules: HgCl_2 , HgCl_3^- , and HgCl_4^{2-} as we move across the series we are successively adding a Cl to the central Hg atom. For each structure how would you expect the Cl atoms to arrange themselves around the Hg atom? Sketch each of the structures to show the shape of the molecule you predict.
- Check you answers by inspecting the corresponding crystal structures. The following structures

are provided: HgCl_2 (refcode *OKAJZO*), HgCl_3^- (refcode *KUSMAM*), and HgCl_4^{2-} (refcode *KEYZUK*). To display a structure type it's reference code (refcode) in the **Entry** box above the structure list on the left hand side of the WebCSD page:



To manipulate structures in the 3D viewer:

1. Structures can be rotated by moving the cursor in the display area while keeping the left-hand mouse button pressed down.
 2. To zoom in and out move the cursor up and down in the display area while keeping both the shift key and the left-hand mouse button pressed down.
 3. To translate structures move the cursor in the display area while keeping both the left-hand mouse button and the keyboard Ctrl key pressed down.
 4. At any stage the display area can be returned to the default view by hitting the *r* button on the keyboard.
- Do the shapes of the experimentally determined structures agree with your predictions? For each of the three structures measure the Cl-Hg-Cl bond angles in the structure. What does this tell you about the observed geometries?

To measure geometric parameters in the 3D viewer:

1. Select the type of measurement you wish to make by right-clicking within the 3D viewer and selecting **Measure**, followed by either **Distances**, **Angles** or **Torsions**

2. Geometrical measurements (intramolecular or intermolecular) can now be made by clicking on e.g., two atoms for a distance, three atoms for an angle or four atoms for a torsion angle.

3. To remove all geometrical measurements from the display right-click within the 3D viewer and select **Measure**, followed by either **Clear distances**, **Clear angles** or **Clear torsions**.

- HgCl_2 is linear with bonds angles of 180 deg., HgCl_3^- exists in a trigonal planar arrangement with bond angles of approximately 120 deg., and HgCl_4^{2-} is tetrahedral with all bond angles approaching 109.5 deg. What is the main factor that determines the geometry that is adopted?

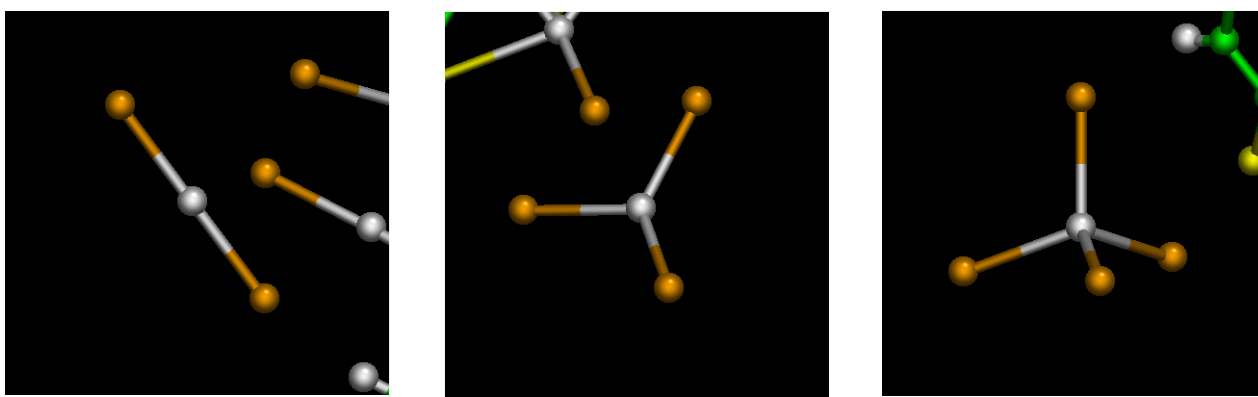
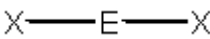
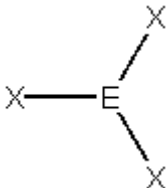
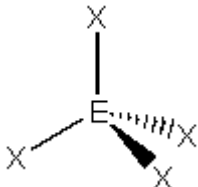
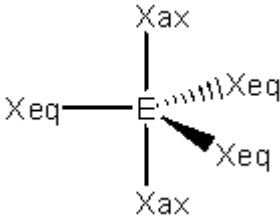
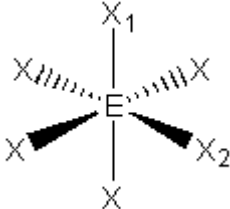
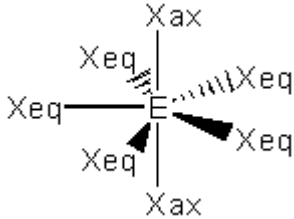
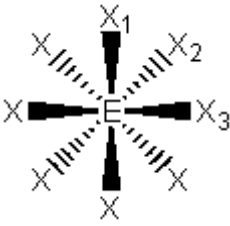


Image: showing HgCl_2 (linear), HgCl_3^- (trigonal planar), and HgCl_4^{2-} (tetrahedral).

1.4.2 The VSEPR model

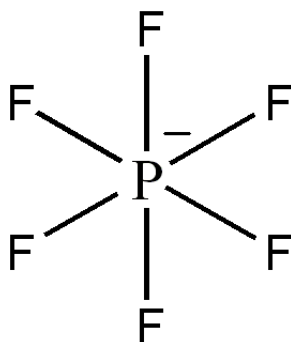
- The valence-shell electron pair repulsion (VSEPR) model is used for predicting molecular shape. The primary assumption of the VSEPR model is that regions of enhanced electron density (i.e. bonding pairs, lone pairs and multiple bonds) take up positions as far apart as possible so that the repulsions between them are minimised.
- Thus, in a molecule EX_n , there is a minimum energy arrangement for a given number of electron pairs. For example, in HgCl_2 repulsions between the two electron pairs in the valence shell of Hg are minimised if the Cl-Hg-Cl unit is linear. In HgCl_3^- electron-electron repulsions are minimised if a trigonal planar arrangement of electron pairs (and thus Cl atoms) is adopted. The table below shows the minimum energy arrangements and ideal bond angles for EX_n molecules (where $n = 2-8$).

Formula EX_n	Number of Electron pairs	Shape	Spatial Arrangement	Ideal Bond Angle (deg.)
EX_2	2	Linear		180
EX_3	3	Trigonal planar		120
EX_4	4	Tetrahedral		109.5
EX_5	5	Trigonal bipyramidal		$X_{ax}-E-X_{eq} = 90$ $X_{eq}-E-X_{eq} = 120$
EX_6	6	Octahedral		$X_1-E-X_2 = 90$
EX_7	7	Pentagonal bipyramidal		$X_{ax}-E-X_{eq} = 90$ $X_{eq}-E-X_{eq} = 72$

Formula EX_n	Number of Electron pairs	Shape	Spatial Arrangement	Ideal Bond Angle (deg.)
EX_8	8	Square Antiprismatic		$\text{X}_1\text{-E-X}_2 = 78$ $\text{X}_1\text{-E-X}_3 = 73$

1.4.3 Apply the VSEPR model to predict basic shape

- The VSEPR model can be applied systematically by following a few simple steps. As an example we will consider the structure of hexafluorophosphate, $[\text{PF}_6]^-$.
- First, draw the Lewis structure of the molecule and identify the central atom. For $[\text{PF}_6]^-$ the central atom is a phosphorus.



- Next, determine the number of valence electrons on the central atom. Phosphorus has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^3$ and thus has 5 valence electrons. Add to this the number of electrons that are contributed by all directly bonded atoms. For $[\text{PF}_6]^-$ there are 6 fluorine atoms, each contributing 1 electron. Finally, we add one electron to account for the single negative charge on the phosphorus. This brings our total to 12.
- Divide this number by 2 to give the total number of electron pairs (i.e. 6) and assign the coordination geometry corresponding to this number using the table in the previous section.
- Hexafluorophosphate, $[\text{PF}_6]^-$ therefore has an octahedral geometry. To summarise:

hexafluorophosphate, $[\text{PF}_6]^-$.	
Central atom:	phosphorus
Valence electrons on central atom:	5
6 F atoms, each contribute 1 electron:	6
Add 1 for negative charge on phosphorus	1
Total:	12
Divide by 2 to give electron pairs:	6
6 electron pairs:	Octahedral geometry for the 6 shape- determining electron pairs

- Check this for yourself by examining the crystal structure of this molecule (refcode *WINFAA*). Measure the F-P-F bond angles in the structure and see how they correspond to the ideal octahedral angles given in the table in the previous section.
- Apply the VSEPR model in order to predict the geometry of the following molecules. Confirm that your answers are correct by examining the corresponding crystal structures. Comment on how closely the observed bond angles agree with the expected ideal values.
 - $[\text{BrF}_6]^-$: refcode *ZAQBIC*
 - $[\text{I}_3]^-$: refcode *RIKTAG*
 - $\text{In}(\text{CH}_3)_3$: refcode *TRMEIN03*
 - $[\text{BeF}_4]^{2-}$: refcode *KIPPEE*
 - $[\text{NH}_4]^+$: refcode *ACARBM01*
 - $\text{Fe}(\text{CO})_5$: refcode *FOJBOV01*
 - $[\text{SbF}_6]^-$: refcode *FUJLAX*

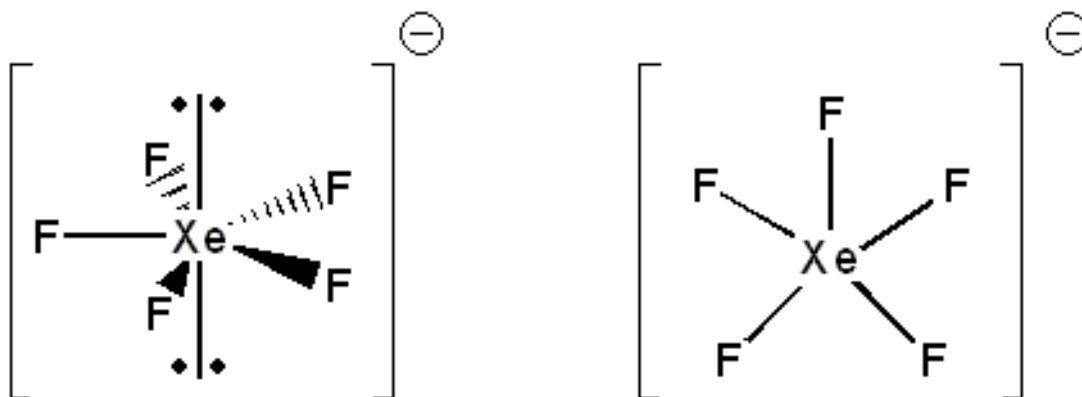
1.4.4 Modifications to basic shapes: considering the effect of lone pairs

- The molecules you have encountered so far include only bonding pairs. How does the presence of lone pairs affect molecular shape?
- Consider the molecule $[\text{XeF}_5]^-$. Xe is in group 18 and possesses 8 electrons in its valence shell. There are 5 fluorine atoms, each contributing 1 electron, this brings our electron count to 13. Finally, we add one electron to account for the single negative charge on the Xe. This brings our total to 14. Again, we divide this number by 2 to give the total number of electron pairs (i.e. 7). The parent shape is therefore a pentagonal bipyramid.
- However, once the basic shape of a molecule has been identified, adjustments must be made to account for the differences in electrostatic repulsion between bonding regions and lone pairs. Repulsions lie in the order:

lone pair/lone pair > lone pair/bonding pair > bonding pair/bonding pair

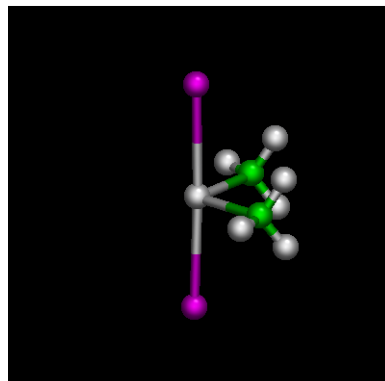
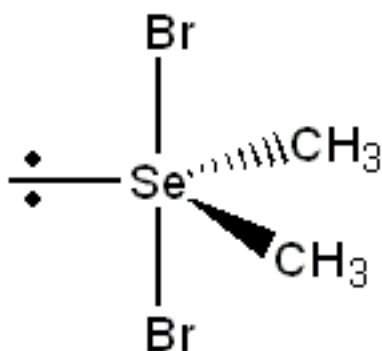
The greater repelling effect of a lone pair is explained by supposing that the lone pair is on average closer to the nucleus than a bonding pair and therefore repels other electrons more strongly.

- Thus for $[\text{XeF}_5]^-$ the parent shape is a pentagonal bipyramid with the lone pairs opposite to each other in order to minimise lone pair/lone pair repulsions. The $[\text{XeF}_5]^-$ anion is therefore pentagonal planar.

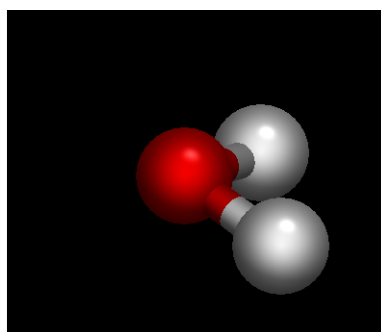
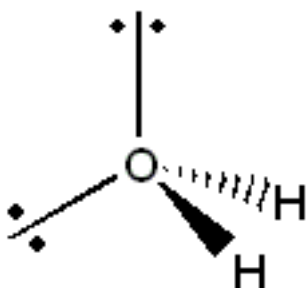


- Check this for yourself by examining the crystal structure of this molecule (refcode *SOBWAH*). Measure the F-Xe-F bond angles in the structure and see how they correspond to the ideal angles given in the table in the previous section.
- Next, examine in detail the crystal structures of di-bromodimethylselenium (refcode *RIZMIW*), and water (refcode *MUSIMO01*). Can you explain the observed shapes of these two molecules in terms of the electrostatic repulsions present?
- Di-bromodimethylselenium (refcode *RIZMIW*) has 5 electron pairs (4 bonding pairs, and 1 lone

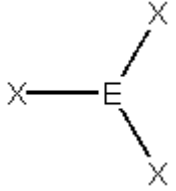
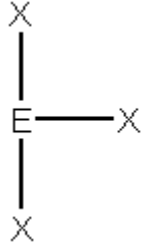
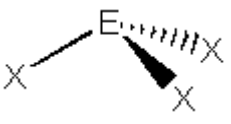
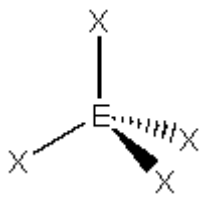


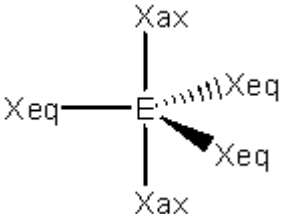
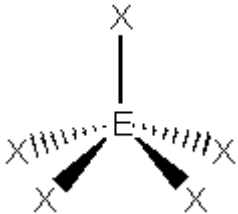
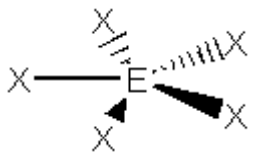
pair), the parent shape is therefore trigonal-bipyramidal. Notice that the lone pair occupies the equatorial site in the trigonal-bipyramidal array. In the equatorial position the lone pair is repelled by two bonding pairs at 90 degrees, whereas in the axial position it would be repelled by 3 bonding pairs at 90 degrees. *RIZMIW* therefore adopts a disphenodial, or “see-saw” shape.



- Water (refcode *MUSIMO01*) has 4 electron pairs (2 bonding pairs and 2 lone pairs). The parent shape is therefore tetrahedral and the molecule will adopt an angular, or “bent” shape. Notice that the HOH angle is decreased relative to that expected when all pairs are bonding. The two lone pairs repel each other more strongly and move apart thus forcing the HOH angle to be less than the ideal tetrahedral angle of 109.5 degrees.



- The table below shows the common shapes for EX_n molecules (where $n = 3-5$) including the shapes adopted by molecules containing one or more lone pairs.

Formula EX_n	Shape		
EX_3	 Trigonal Planar	 T-Shaped	 Trigonal Pyramidal
	 Tetrahedral	 See-Saw (Disphenoidal)	 Square Planar
	 Trigonal bipyramidal	 Square-Based Pyramidal	 Pentagonal Planar

1.4.5 Further examples

- Apply the VSEPR model in order to predict the geometry of the following molecules. Confirm that your answers are correct by examining the corresponding crystal structures. Comment on how closely the observed bond angles agree with the expected ideal values? Can you account for any deviation from the ideal values?
 - Sulfur dioxide: refcode *DADXOW*
 - $[CeCl_6]^{2-}$: refcode *CLCAME01*
 - Dichloro-trifluoromethyl)iodine : refcode *COXYIX*

- NH_3 : refcode *KATLAT*
- Dibromo-pentapyridyl-strontium(ii): refcode *TANWAG*
- $[\text{BCl}_4]^-$: refcode *PETKAB*
- Dichloro-diphenyl-selenium: refcode *PHSECL01*
- trans-bis(Isothiocyanato)-bis(trimethylphosphine)-nickel(ii): refcode *BAZSUR*
- Boric acid: refcode *JAGREP*
- $[\text{ClF}_4]^-$: refcode *ROLSEQ*
- Pentaphenoxyphosphorane: refcode *PPHOXP*
- $[\text{SbBr}_5]^{2-}$: refcode *CLPYSB*
- tris(Acetonitrile)-trichloro-titanium acetonitrile: refcode *DUDKUII0*
- bis(1,2,3,4,5,6,7,8-Octaethylporphyrinato-N,N,N,N)-cerium(iv): refcode *DURLUX*

1.5 SUMMARY OF KEY CONCEPTS

- The valence-shell electron pair repulsion (VSEPR) model is used for predicting molecular shape. The primary assumption of the VSEPR model is that regions of enhanced electron density (i.e. bonding pairs, lone pairs and multiple bonds) take up positions as far apart as possible so that the repulsions between them are minimised.
- Once the basic shape of a molecule has been identified, adjustments must be made to account for the differences in electrostatic repulsion between bonding regions and lone pairs. Repulsions lie in the order:

lone pair/lone pair > lone pair/bonding pair > bonding pair/bonding pair

Thus for $[\text{XeF}_5]^-$ the parent shape is a pentagonal bipyramid with the lone pairs opposite to each other in order to minimise lone pair/lone pair repulsions. The $[\text{XeF}_5]^-$ anion is therefore pentagonal planar.

- A deficiency of the VSEPR model is that it cannot be used to predict the actual bond angle adopted by the molecule. For example, the HOH angle in water is decreased relative to that expected when all 4 electron pairs are bonding. The two lone pairs repel each other more strongly and move apart thus forcing the HOH angle to be less than the ideal tetrahedral angle of 109.5 degrees.