The Valence Shell Electron Pair Repulsion (VSEPR) theory is a simple and useful way to predict and rationalize the shapes of molecules. The theory is based on the idea of minimizing the electrostatic repulsion between electron pairs.

To use the VSEPR model, one begins with the Lewis dot picture to determine the number of lone pairs and bonding domains around a central atom. Because VSEPR considers all bonding domains equally (i.e., a single bond, a double bond, and a half bond all count as one electron domain), one can use either an octet or hypervalent structure, provided that the number of lone pairs (which should be the same in both) is calculated correctly. For example, in either the hypervalent or octet structure of the \( \text{I}_3^- \) ion calculated in the previous section, there are three lone pairs on the central I atom and two bonding domains. We then follow these steps to obtain the electronic geometry:

- Determine the number of lone pairs on the central atom in the molecule, and add the number of bonded atoms (a.k.a. bonding domains)
- This number (known as the steric number) defines the electronic shape of the molecule by minimizing repulsion. For example, a steric number of three gives a trigonal planar electronic shape.
- The angles between electron domains are determined primarily by the electronic geometry (e.g., \(109.5^\circ\) for a steric number of 4, which implies that the electronic shape is a tetrahedron)
- These angles are adjusted by the hierarchy of repulsions: (lone pair - lone pair) > (lone pair - bond) > (bond - bond)

**Note**

The hierarchy of repulsions can also be used to rationalize which sites lone pairs and ligands occupy in molecules with a large steric number and few ligands/many lone pairs. This can be observed in the table below and is further covered below in the geometrical isomers subsection with the \( \text{XeF}_2 \) molecule.

![Figure 1.2.1: Geometry of the Water Molecule](image)

The **molecular geometry** is deduced from the electronic geometry by considering the lone pairs to be present but invisible. The most commonly used methods to determine molecular structure - X-ray diffraction, neutron diffraction, and electron diffraction - have a hard time seeing lone pairs, but they can accurately determine the lengths of bonds between atoms and the bond angles. Table 1.2.1 gives examples of electronic and molecular shapes for steric numbers between 2 and 9.
<table>
<thead>
<tr>
<th>Bonding electron pairs</th>
<th>Lone pairs</th>
<th>Electron domains (Steric #)</th>
<th>Shape</th>
<th>Ideal bond angle (example’s bond angle)</th>
<th>Example</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>linear</td>
<td>$\langle 180^\circ \rangle$</td>
<td>(CO$_2$)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3</td>
<td>trigonal planar</td>
<td>$\langle 120^\circ \rangle$</td>
<td>(BF$_3$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3</td>
<td>bent</td>
<td>$\langle 120^\circ \rangle$, $\langle 119^\circ \rangle$</td>
<td>(SO$_2$)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>4</td>
<td>tetrahedral</td>
<td>$\langle 109.5^\circ \rangle$</td>
<td>(CH$_4$)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4</td>
<td>trigonal pyramidal</td>
<td>$\langle 109.5^\circ \rangle$, $\langle 107^\circ \rangle$</td>
<td>(NH$_3$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4</td>
<td>bent</td>
<td>$\langle 109.5^\circ \rangle$, $\langle 104.5^\circ \rangle$</td>
<td>(H$_2$O)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>$\langle 90^\circ \rangle$, $\langle 120^\circ \rangle$, $\langle 180^\circ \rangle$</td>
<td>(PCl$_5$)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>5</td>
<td>seesaw</td>
<td>$\langle 180^\circ \rangle$, $\langle 120^\circ \rangle$, $\langle 90^\circ \rangle$, $\langle 173.1^\circ \rangle$, $\langle 101.6^\circ \rangle$</td>
<td>(SF$_4$)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5</td>
<td>T-shaped</td>
<td>$\langle 90^\circ \rangle$, $\langle 180^\circ \rangle$, $\langle 87.5^\circ \rangle$, $&lt; \langle 180^\circ \rangle$</td>
<td>(ClF$_3$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5</td>
<td>linear</td>
<td>$\langle 180^\circ \rangle$</td>
<td>(XeF$_2$)</td>
<td></td>
</tr>
<tr>
<td>Bonding electron pairs</td>
<td>Lone pairs</td>
<td>Electron domains (Steric #)</td>
<td>Shape</td>
<td>Ideal bond angle (example's bond angle)</td>
<td>Example</td>
<td>Image</td>
</tr>
<tr>
<td>------------------------</td>
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<td>-------------------------------</td>
<td>-------------------</td>
<td>----------------------------------------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>6</td>
<td>octahedral</td>
<td>((90^\circ, 180^\circ))</td>
<td>((SF_6))</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>6</td>
<td>square pyramidal</td>
<td>((90^\circ, 84.8^\circ, 180^\circ))</td>
<td>((BrF_5))</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>6</td>
<td>square planar</td>
<td>((90^\circ, 180^\circ))</td>
<td>((XeF_4))</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>7</td>
<td>pentagonal bipyramidal</td>
<td>((90^\circ, 72^\circ, 180^\circ))</td>
<td>((IF_7))</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>7</td>
<td>pentagonal pyramidal</td>
<td>((72^\circ, 90^\circ, 144^\circ))</td>
<td>((XeOF_5^-))</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>7</td>
<td>planar pentagonal</td>
<td>((72^\circ, 144^\circ))</td>
<td>((XeF_5^-))</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>8</td>
<td>square antiprismatic</td>
<td>((XeF_8^{2-}))</td>
<td>((XeF_8^{2-}))</td>
<td><img src="image7.png" alt="Image" /></td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>9</td>
<td>tricapped trigonal prismatic</td>
<td></td>
<td>((ReH_9^{2-}))</td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>

From Table 1.2.1, we see that some of the molecules shown as examples have bond angles that depart from the ideal electronic geometry. For example, the \((H-N-H)\) bond angle in ammonia is \((107^\circ)\), and the \((H-O-H)\) angle in water is \((104.5^\circ)\). We can rationalize this in terms of the last rule above. The lone pair in ammonia repels the electrons in the \((N-H)\) bonds more than the bonding electrons repel each other. This lone pair repulsion exerts even more steric influence in the case of water, where there are two lone pairs. Similarly, the axial \((F-S-F)\) angle in the "bent-T" molecule \((SF_4)\) is a few degrees less than \((180^\circ)\) because of repulsion by the lone pair in the molecule.
Geometrical Isomers

For some molecules in Table 1.2.1, we note that there is more than one possible shape that would satisfy the VSEPR rules. For example, the \(\text{XeF}_2\) molecule has a steric number of five and a trigonal bipyramidal geometry. There are three possible stereoisomers: one in which the \(\text{F}\) atoms occupy axial sites, resulting in linear molecule, one in which the \(\text{F}\) atoms occupy one equatorial and one axial site (resulting in a \(90^\circ\)) bond angle), and one in which the \(\text{F}\) atoms are both on equatorial sites, with a \(\text{F-Xe-F}\) bond angle of \(120^\circ\).

Let us consider the non-linear stereoisomers first. If we were to place one of the Fluorines equatorial (whilst maintaining the trigonal bipyramidal structure of the electron domains of the central Xenon atom) we would get a structure where one of the lone pairs is axial and the other two are equatorial. This means that the axial lone pair would have an angle of \(90^\circ\) with the equatorial lone pairs, and the equatorial lone pairs would have an angle of \(120^\circ\) among themselves. This is highly unfavourable as the lone pairs are bunched close together. If we were to place both Fluorines equatorial (once again maintaining the trigonal bipyramidal structure of the electron domains of the central Xenon atom), we get a structure where there are two axial lone pairs and one equatorial lone pair. In this structure the axial lone pairs have an angle of \(180^\circ\) among themselves, but (like the previous structure) form an angle of \(90^\circ\) with the equatorial lone pair. This is unfavourable as well (though slightly more favorable than the previous scenario). Placing all the lone pairs equatorial yields a 120 degree angle in between all the lone pairs and thus maximizes the distance between them. This leads to the linear molecule which is the most stable (something we confirm by the fact that it is the only experimentally observable isomer of \(\text{XeF}_2\)).

**Figure 1.2.2: \(\text{XeF}_2\) Geometry**

Note

Angles used in the preceding discussion were geometrically determined as the other isomers of \(\text{XeF}_2\) are non existent and thus we have no actual measure of their bond angles.

Example 1.2.1: The \(\text{BrF}_4^-\) Interhalide Ion

In the case of the \(\text{BrF}_4^-\) anion, which is isoelectronic with \(\text{XeF}_4\) in Table 1.2.1, the electronic geometry is octahedral and there are two possible isomers in which the two lone pairs are cis or trans to each other. In this case, lone pair - lone pair repulsion dominates and we obtain the trans arrangement of lone pairs, giving a square planar molecular geometry.
Orbital Hybridization

The observation of molecules in the various electronic shapes shown above is, at first blush, in conflict with our picture of atomic orbitals. For an atom such as oxygen, we know that the \(2s\) orbital is spherical, and that the \(2p_x\), \(2p_y\), and \(2p_z\) orbitals are dumbbell-shaped and point along the Cartesian axes (Figure 1.2.4). The water molecule contains two hydrogen atoms bound to oxygen not at a \(90^\circ\) angle, but at an angle of \(104.5^\circ\). Given the relative orientations of the atomic orbitals, how do we arrive at angles between electron domains of \(104.5^\circ\), \(120^\circ\), and so on?

The atomic orbitals \(\psi\) represent solutions to the Schrödinger wave equation, which for hydrogen-like (one-electron) atoms can be written as:

\[
E \psi = -\dfrac{\hbar^2}{2\mu} \nabla^2 \psi - \dfrac{Ze^2}{4\pi\epsilon_0 r}\psi
\tag{1.2.1}
\]

where

- \(Z\) is the nuclear charge,
- \(e\) is the electron charge, and
- \(r\) is the position of the electron.

The radial potential term on the right side of the equation is due to the Coulomb interaction, in which \(\epsilon_0\) is the electric constant (permittivity of free space) and
\[
\mu = \frac{m_e m_n}{m_e + m_n} \tag{1.2.2}
\]

is the 2-body reduced mass of the nucleus of mass \(m_n\) and the electron of mass \(m_e\). To a good approximation, \(\mu \approx m_e\).

Without going into too much detail about the Schrödinger equation, we can point out some of its most important properties:

- The Schrödinger equation is a differential equation, in which the Laplacian operator \((\nabla^2)\) takes the second derivative (with respect to three spatial coordinates) of the wavefunction \(\psi\).
- The solutions to the Schrödinger equation are a set of energies \(E\) (which are scalar quantities) and wavefunctions (a.k.a. atomic orbitals) \(\psi\), which are functions of the spatial coordinates \(\{x\}, \{y\}, \{z\}\). You will sometimes see the energies referred to as eigenvalues and the orbitals as eigenfunctions, because mathematically the Schrödinger equation is an eigenfunction-eigenvalue equation. Although \(\psi\) is a function of the coordinates, \(E\) is not. So an electron in a \(2p_z\) orbital has the same total energy \(E\) (\(\approx PE + KE\)) no matter where it is.
- These \(E\) values and their associated wavefunctions \(\psi\) are catalogued according to their quantum numbers \(n, l, m_l\). That is, there are many solutions to the differential equation, and each solution \(\psi\) has a unique set of quantum numbers. Some sets of orbitals are degenerate, meaning that they have the same energy (e.g., \(2p_x, 2p_y, 2p_z\)).
- The solutions \(\psi\) to the Schrödinger equation (e.g., the \(\{1s\}, \{2s\}, \{2p_x\}, \{2p_y\}, \{2p_z\}\) orbitals) represent probability amplitudes for finding the electron at a particular point \((x,y,z)\) in space. A probability amplitude can have either + or - sign. We typically represent the different signs by shading or by + and - signs on the two lobes of a \(2p\) orbital.
- The square of the probability amplitude, \(\psi^2\), is always a positive number and represents the probability of finding the electron at a point \(x,y,z\) in space. Because the total probability of finding the electron somewhere is 1, the wavefunction must be normalized so that the integral of \(\psi^2\) over the spatial coordinates (from \(-\infty\) to \(+\infty\)) is 1.
- The solutions to the Schrödinger equation are orthogonal, meaning that the product of any two (integrated over all space) is zero. For example, the product of the \(\{2s\}\) and \(\{2p_x\}\) orbitals, integrated over the spatial coordinates from \(-\infty\) to \(+\infty\), is zero.

Orbital hybridization involves making linear combinations of the atomic orbitals that are solutions to the Schrödinger equation. Mathematically, this is justified by recognizing that the Schrödinger equation is a linear differential equation. As such, any sum of solutions to the Schrödinger equation is also a valid solution. However, we still impose the constraint that our hybrid orbitals must be orthogonal and normalized.

**Rules for orbital hybridization:**

- Add and subtract atomic orbitals to get hybrid orbitals.
- We get the same number of orbitals out as we put in.
- The energy of a hybrid orbital is the weighted average of the atomic orbitals that make it up.
- The coefficients are determined by the constraints that the hybrid orbitals must be orthogonal and normalized.

\((sp)\) Hybridization

For \((sp)\) hybridization, as in the \((BeF_2)\) or \((CO_2)\) molecule, we make two linear combinations of the \(\{2s\}\) and \(\{2p_z\}\) orbitals (assigning \(z\) as the axis of the \((Be-F)\) bond):

- \(\{1s\}\) orbital is used to form the \(\sigma\) bond.
- The \(\pi\) bond is formed by the \(\{2p_x\}\) and \(\{2p_y\}\) orbitals.
Here we have simply added and subtracted the $2s$ and $2p_z$ orbitals; we leave it as an exercise for the interested student to show that both orbitals are normalized (i.e., $\psi_1^2=\psi_2^2=1$) and orthogonal ($\psi_1\psi_1=0$).

What this means physically is explained in the figure below. By combining the $2s$ and $2p_z$ orbitals we have created two new orbitals with large lobes (high electron probability) pointing along the z-axis. These two orbitals are degenerate and have an energy that is halfway between the energy of the $2s$ and $2p_z$ orbitals.

**Figure 1.2.4:** Linear combinations of the $2s$ and $2p_z$ atomic orbitals make two $2sp_z$ hybrids. The $2p_x$ and $2p_y$ orbitals are unchanged.

For an isolated $Be$ atom, which has two valence electrons, the lowest energy state would have two electrons spin-paired in the $2s$ orbital. However, these electrons would not be available for bonding. By promoting these electrons to the degenerate $2sp_z$ hybrid orbitals, they become unpaired and are prepared for bonding to the $F$ atoms in $BeF_2$. This will occur if the bonding energy (in the promoted state) exceeds the promotion energy. The overall bonding energy, i.e., the energy released by combining a $Be$ atom in its ground state with two $F$ atoms, is the difference between the bonding and promotion energies.

**$sp^2$ hybridization**

We can similarly construct $sp^2$ hybrids (e.g., for the $BF_3$ molecule or the $NO_3^-$ anion) from one $2s$ and two $2p$ atomic orbitals. Taking the plane of the molecule as the xy plane, we obtain three hybrid orbitals at $120^\circ$ to each other. The three hybrids are:

$$\psi_1 = \frac{1}{\sqrt 3}(2s)+\frac{\sqrt 2}{\sqrt 3}(2p_x) \tag{1.2.4a}$$

$$\psi_2 = \frac{1}{\sqrt 3}(2s)-\frac{1}{\sqrt 6}(2p_x)+\frac{1}{\sqrt 2}(2p_y) \tag{1.2.4b}$$

$$\psi_3 = \frac{1}{\sqrt 3}(2s)-\frac{1}{\sqrt 6}(2p_x)-\frac{1}{\sqrt 2}(2p_y) \tag{1.2.4c}$$
These orbitals are again degenerate and their energy is the weighted average of the energies of the \(2s\), \(2p_x\), and \(2p_y\) atomic orbitals.

**(sp\(^3\)) hybridization**

Finally, to make a \(\text{(sp}^3\)) hybrid, as in \(\text{(CH}_4\text{)}, \text{(H}_2\text{O}\text{)},\) etc., we combine all four atomic orbitals to make four degenerate hybrids:

\[
\psi_1 = \dfrac{1}{2}(2s+2p_x+2p_y+2p_z) \tag{1.2.5a}\]
\[
\psi_2 = \dfrac{1}{2}(2s-2p_x-2p_y+2p_z) \tag{1.2.5b}\]
\[
\psi_3 = \dfrac{1}{2}(2s+2p_x-2p_y-2p_z) \tag{1.2.5c}\]
\[
\psi_4 = \dfrac{1}{2}(2s-2p_x+2p_y-2p_z) \tag{1.2.5d}\]

The lobes of the \(\text{(sp}^3\)) **hybrid** orbitals point towards the vertices of a tetrahedron (or alternate corners of a cube), consistent with the tetrahedral bond angle in \(\text{(CH}_4\text{)}\) and the nearly tetrahedral angles in \(\text{(NH}_3\text{)}\) and \(\text{(H}_2\text{O}\text{)}\). Similarly, we can show that we can construct the trigonal bipyramidal electronic shape by making \(\text{(sp)}\) and \(\text{(sp}^2\)) hybrids, and the octahedral geometry from three sets of \(\text{(sp)}\) hybrids. The picture that emerges from this is that the atomic orbitals can hybridize as required by the shape that best minimizes electron pair repulsions.
Interestingly however, the bond angles in \((\text{PH}_3)\), \((\text{H}_2\text{Si})\) and \((\text{H}_2\text{Se})\) are close to \((90^\circ)\), suggesting that \((\text{P})\), \((\text{S})\), and \((\text{Se})\) primarily use their \((p)\)-orbitals in bonding to \((\text{H})\) in these molecules. This is consistent with the fact that the energy difference between \((s)\) and \((p)\) orbitals stays roughly constant going down the periodic table, but the bond energy decreases as the valence electrons get farther away from the nucleus. In compounds of elements in the 3rd, 4th, and 5th rows of the periodic table, there thus is a decreasing tendency to use \((s-p)\) orbital hybrids in bonding. For these heavier elements, the bonding energy is not enough to offset the energy needed to promote the \((s)\) electrons to \((s-p)\) hybrid orbitals.

Contributors

- Adapted from the Wikibook constructed by Chemistry 310 students at Penn State University.