Refinement of VSEPR theory predicted geometries

The relative steric demand of objects will alter the arrangement of the atoms around the central atom.

Valence Bond Theory

Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy directed orbitals localized on a particular atom. The directionality of the orbitals is determined by the geometry around the atom which is obtained from the predictions of VSEPR theory.

In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.
Valence Bond Theory

Detailed valence bond theory treatment of bonding in $\text{H}_2$.

$\phi_A (1) \quad \phi_B (2)$

VBT considers the interactions between separate atoms as they are brought together to form molecules.

$\Psi_1 = \phi_A(1) \phi_B(2)$

Quantum mechanics demands that electrons can be interchangeable so we must use a linear combination of $\Psi_1$ and $\Psi_2$.

$\Psi_2 = \phi_A(2) \phi_B(1)$

$\Psi_1 = N (\Psi_1 + \Psi_2)$ (bonding, H-H)

$\Psi_2 = N (\Psi_1 - \Psi_2)$ (anti-bonding)

$\Psi_3 = \phi_A(1) \phi_A(2)$ (ionic H-H$^+$)

$\Psi_4 = \phi_B(1) \phi_B(2)$ (ionic H$^+$ H$^-$)

$N$ is a normalizing coefficient
$C$ is a coefficient related to the amount of ionic character

$\Psi_{\text{molecule}} = N [\Psi_1 + \Psi_2] + (C [\Psi_3 + \Psi_4])$

$\Psi_{\text{molecule}} = N [\Psi_{\text{covalent}} + (C \Psi_{\text{ionic}})]$

Valence Bond Theory

Valence bond theory treatment of bonding in $\text{H}_2$ and $\text{F}_2$ – the way we will use it.

This gives a 1s-1s $\sigma$ bond between the two H atoms.

For VBT treatment of bonding, we will ignore the anti-bonding combinations and the ionic contributions.
Valence bond theory treatment of bonding in O₂

This gives a 2p-2p σ bond between the two O atoms.

This gives a 2p-2p π bond between the two O atoms. In VBT, π bonds are predicted to be weaker than σ bonds because there is less overlap.

The Lewis approach and VBT predict that O₂ is diamagnetic – this is wrong!

Directionality

The bonding in diatomic molecules is adequately described by combinations of “pure” atomic orbitals on each atom. The only direction that exists in such molecules is the inter-nuclear axis and the geometry of each atom is undefined in terms of VSEPR theory (both atoms are terminal). This is not the case with polyatomic molecules and the orientation of orbitals is important for an accurate description of the bonding and the molecular geometry.

Examine the predicted bonding in ammonia using “pure” atomic orbitals:

The 2p orbitals on N are oriented along the X, Y, and Z axes so we would predict that the angles between the 2p-1s σ bonds in NH₃ would be 90°. We know that this is not the case.
Hybridization

The problem of accounting for the true geometry of molecules and the directionality of orbitals is handled using the concept of hybrid orbitals. Hybrid orbitals are mixtures of atomic orbitals and are treated mathematically as linear combinations of the appropriate s, p and d atomic orbitals.

**Linear sp hybrid orbitals**

A 2s orbital superimposed on a 2px orbital

\[ \Psi_1 = \frac{1}{\sqrt{2}} \phi_s + \frac{1}{\sqrt{2}} \phi_p \]

\[ \Psi_2 = \frac{1}{\sqrt{2}} \phi_s - \frac{1}{\sqrt{2}} \phi_p \]

The 1/\sqrt{2} are normalization coefficients.

Orthogonality and Normalization

Two properties of acceptable orbitals (wavefunctions) that we have not yet considered are that they must be orthogonal to every other orbital and they must be normalized. These conditions are related to the probability of finding an electron in a given space.

Orthogonal means that the integral of the product of an orbital with any other orbital is equal to 0, i.e.:

\[ \int \Psi_n \Psi_m \partial \tau = 0 \]

where \( n \neq m \) and \( \partial \tau \) means that the integral is taken over “all of space” (everywhere).

Normal means that the integral of the product of an orbital with itself is equal to 1, i.e.:

\[ \int \Psi_n \Psi_n \partial \tau = 1 \]

This means that we must find normalization coefficients that satisfy these conditions. Note that the atomic orbitals (\( \phi \)) we use can be considered to be both orthogonal and normal or “orthonormal.”
Example of the orthogonality of $\Psi_1$ and $\Psi_2$

\[ \Psi_1 = \frac{1}{\sqrt{2}} \phi_s + \frac{1}{\sqrt{2}} \phi_p \quad \Psi_2 = \frac{1}{\sqrt{2}} \phi_s - \frac{1}{\sqrt{2}} \phi_p \]

\[ \int \Psi_1^* \Psi_2 \, d\tau = \int \left( \frac{1}{\sqrt{2}} \phi_s + \frac{1}{\sqrt{2}} \phi_p \right) \left( \frac{1}{\sqrt{2}} \phi_s - \frac{1}{\sqrt{2}} \phi_p \right) \, d\tau \]

\[ \int \Psi_1^* \Psi_2 \, d\tau = \frac{1}{2} \int (\phi_s \phi_s) \, d\tau - \frac{1}{2} \int (\phi_s \phi_p) \, d\tau + \frac{1}{2} \int (\phi_p \phi_s) \, d\tau - \frac{1}{2} \int (\phi_p \phi_p) \, d\tau \]

\[ \int \Psi_1^* \Psi_2 \, d\tau = \frac{1}{2} (1) - \frac{1}{2} (0) + \frac{1}{2} (0) - \frac{1}{2} (1) \]

\[ \int \Psi_1^* \Psi_2 \, d\tau = \frac{1}{2} - \frac{1}{2} = 0 \]

Thus our hybrid sp orbitals are orthogonal to each other, as required.

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**Hybridization**

Valence bond theory treatment of a linear molecule: the bonding in BeH$_2$

BeH$_2$

Be

\[ \uparrow \quad \uparrow \quad \quad \downarrow \quad \downarrow \]

2s

2p

Be$^*$

\[ \uparrow \quad \quad \quad \quad \quad \quad \uparrow \quad \quad \quad \quad \quad \quad \downarrow \quad \downarrow \]

2p

sp

Be$^*$ (sp)

\[ \uparrow \quad \uparrow \quad \uparrow \quad \quad \downarrow \quad \downarrow \]

Be$^*$ (sp)

\[ \uparrow \quad \uparrow \quad \uparrow \quad \quad \downarrow \quad \downarrow \]

2H

\[ \downarrow \quad \downarrow \]

1s

1s

H−Be−H

The promotion energy can be considered a part of the energy required to form hybrid orbitals.

The overlap of the hybrid orbitals on Be with the 1s orbitals on the H atoms gives two Be-H (sp)-1s $\sigma$ bonds oriented 180° from each other. This agrees with the VSEPR theory prediction.
Valence bond theory treatment of a trigonal planar molecule: the bonding in BH₃

This gives three sp² orbitals that are oriented 120° apart in the xy plane – be careful: the choice of axes in this example determines the set of coefficients.

The coefficients in front of each atomic wavefunction indicate the amount of each atomic orbital that is used in the hybrid orbital. The sign indicates the orientation (direction) of the atomic orbitals. Remember that you have to use each atomic orbital completely (columns) and that each hybrid must be normal (rows). Check this by summing the squares of the coefficients.
Valence bond theory treatment of a trigonal planar molecule: the bonding in BH₃

The overlap of the sp² hybrid orbitals on B with the 1s orbitals on the H atoms gives three B-H (sp²)-1s σ bonds oriented 120° from each other. This agrees with the VSEPR theory prediction.

Valence bond theory treatment of a tetrahedral molecule: the bonding in CH₄

This gives four sp³ orbitals that are oriented in a tetrahedral fashion.
Valence bond theory treatment of a tetrahedral molecule: the bonding in CH₄

The overlap of the sp³ hybrid orbitals on C with the 1s orbitals on the H atoms gives four C-H (sp³)-1s σ bonds oriented 109.47° from each other. This provides the tetrahedral geometry predicted by VSEPR theory.

Valence bond theory treatment of a trigonal bipyramidal molecule: the bonding in PF₅

PF₅ has an VSEPR theory AX₅E₅ geometry so we need hybrid orbitals suitable for bonds to 5 atoms. ns and np combinations can only provide four, so we need to use nd orbitals (if they are available).

The appropriate mixture to form a trigonal bipyramidal arrangement of hybrids involves all the ns and np orbitals as well as the nd₂ orbital.
Valence bond theory treatment of a trigonal bipyramidal molecule

The orbitals are treated in two different sets.

$$\Psi_1 = \frac{1}{\sqrt{3}} \phi_s + \frac{1}{\sqrt{6}} \phi_p + \frac{1}{\sqrt{2}} \phi_d$$

$$\Psi_2 = \frac{1}{\sqrt{3}} \phi_s + \frac{1}{\sqrt{6}} \phi_p - \frac{1}{\sqrt{2}} \phi_d$$

$$\Psi_3 = \frac{1}{\sqrt{3}} \phi_s - \frac{2}{\sqrt{6}} \phi_p$$

These coefficients are exactly the same as the result for the trigonal planar molecules because they are derived from the same orbitals (sp$^2$).

$$\Psi_4 = \frac{1}{\sqrt{2}} \phi_p + \frac{1}{\sqrt{2}} \phi_d$$

$$\Psi_5 = -\frac{1}{\sqrt{2}} \phi_p + \frac{1}{\sqrt{2}} \phi_d$$

These coefficients are similar to those for the sp hybrids because they are formed from a combination of two orbitals (pd).

Remember that d orbitals are more diffuse than s or p orbitals so VBT predicts that the bonds formed by hybrids involving d orbitals will be longer than those formed by s and p hybrids.

Valence bond theory treatment of a trigonal bipyramidal molecule: the bonding in PF$_5$

The overlap of the sp$^3$d hybrid orbitals on P with the 2p orbitals on the F atoms gives five P-F (sp$^3$d)-2p $\sigma$ bonds in two sets: the two axial bonds along the z-axis (180° from each other) and three equatorial bonds in the xy plane (120° from each other and 90° from each axial bond). This means that the 5 bonds are not equivalent!
The square pyramidal AX₅ geometry requires mixing with a different d orbital than in the trigonal bipyramidal case.

You should consider what orbital(s) would be useful for such a geometry and we will see a way to figure it out unambiguously when we examine the symmetry of molecules.

Valence bond theory treatment of an octahedral molecule: the bonding in SF₆

The overlap of the sp³d² hybrid orbitals on S with the 2p orbitals on the F atoms gives six S-F (sp³d²)-2p σ bonds 90° from each other that are equivalent. You can figure out the normalization coefficients.
Valence bond theory treatment of $\pi$-bonding: the bonding in ClNO

There are three “objects” around N so the geometry is trigonal planar. The shape is given by $AX_2E$ (angular or bent).

The overlap of the sp$^2$ hybrid orbitals on N with the 3p orbital on Cl and the 2p orbital on O give the two $\sigma$ bonds and it is the overlap of the “left over” p orbital on N with the appropriate orbital on O that forms the (2p-2p) $\pi$ bond between the two atoms.

Valence bond theory treatment of $\pi$-bonding: the bonding in the nitrate anion

There are three “objects” around N so the geometry is trigonal planar. The shape is given by $AX_3$ (trigonal planar).

The overlap of the sp$^2$ hybrid orbitals on N with the the 2p orbitals on the O give the three (sp$^2$-2p) $\sigma$ bonds and it is the overlap of the “left over” p orbital on N with the appropriate orbital on the uncharged O atom that forms the (2p-2p) $\pi$ bond.
Valence bond theory treatment of π-bonding: the bonding in ethene

Each C

\[ \begin{array}{c}
\text{2s} \\
\uparrow \\
\text{2p} \\
\uparrow \\
\end{array} \]

Each C*

\[ \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array} \]

C*(sp\(^2\))

\[ \begin{array}{c}
\text{sp}\(^2\) \\
\uparrow \\
\uparrow \\
\uparrow \\
2p \\
\uparrow \\
\sigma \\
\sigma \\
\sigma \\
\sigma \\
\end{array} \]

There are three “objects” around each C so the geometry is trigonal planar at each carbon. The shape is given by AX\(_3\) for each carbon.

4 H

\[ \begin{array}{c}
\text{1s} \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array} \]

The overlap of the sp\(^2\) hybrid orbitals on C with the 1s orbitals on each H give the four terminal (sp\(^2\)-1s) \(\sigma\) bonds. The double bond between the C atoms is formed by a (sp\(^2\)-sp\(^2\)) \(\sigma\) bond and the (2p-2p) \(\pi\) bond.

Valence bond theory treatment of π-bonding: the bonding in SOCl\(_2\)

S

\[ \begin{array}{c}
\text{3s} \\
\uparrow \\
\text{3p} \\
\uparrow \\
\end{array} \]

S*

\[ \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array} \]

S*(sp\(^3\))

\[ \begin{array}{c}
\text{sp}\(^3\) \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\text{3d} \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\sigma \\
\sigma \\
\sigma \\
\sigma \\
\uparrow \\
\sigma \\
\uparrow \\
\end{array} \]

There are four “objects” around S so the geometry is tetrahedral and the shape is given by AX\(_3\)E (pyramidal).

Cl Cl O

\[ \begin{array}{c}
\text{2s} \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array} \]

\[ \begin{array}{c}
\text{2p} \\
\uparrow \\
\end{array} \]

The overlap of the sp\(^3\) hybrid orbitals on S with the 3p orbitals on Cl and the 2p orbital on O give the three \(\sigma\) bonds and, because the lone pair is located in the final sp\(^3\) hybrid, it is the overlap of the “left over” d orbital on S with an appropriate p orbital on O that forms the (3d-2p) \(\pi\) bond in the molecule.
Valence bond theory treatment of bonding: a hypervalent molecule, ClF₃

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<th>3s</th>
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<td>Cl*</td>
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<td>Cl* (sp³d)</td>
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The overlap of the sp³d hybrid orbitals on Cl with the 2p orbitals on the F atoms gives three P-F (sp³d)-2p σ bonds in two sets: the two axial bonds along the z-axis (less than 180° from each other because of the repulsion from the lone pairs) and the one equatorial bond halfway between the other Cl bonds. Again, the bond lengths will not be the same because there is more d contribution to the axial hybrid orbitals.

There are five “objects” around Cl so the geometry is trigonal bipyramidal and the shape is given by AX₃E₂ (T-shaped). Consider this: Why are such molecules T-shaped instead of pyramidal?

Summary of Valence Bond Theory

1. Write an acceptable Lewis structure for the molecule.

   H—Be—H

   Two objects around Be, so AX₂ (linear)

2. Determine the number of VSEPR objects around all central atoms and determine the geometry around the atom.

   Two orbitals pointing 180° from each other needed, so use two sp hybrids

3. Construct hybrid orbitals suitable for the predicted bonding.

   Two (sp-1s) Be-H σ bonds.

4. Link orbitals together to make bonds.

5. Describe the bonding. Include the names of the orbitals involved in each bond. Draw pictures of the bonds formed by the overlap of these orbitals.