10/09/14

~~Valence~~ Bond Theory

why?

↳ $\psi \xrightarrow{\hat{\Omega}}$ Energies, Structures, Reactivities → Chemical properties

↳ Complex chemical species requires shortcuts.

- VBT & MO Theory to describe bonding based on atomic understanding of ψ.

↳ Semi-quantitative approach.

↳ qualitative (high-school): VSEPR → limited chemical insight

↳ quantitative (grad school): var. principle. ↳ computationally practical.

Valence Bond Theory

1. Assume only valence (or near valence) atomic orbitals participate in bonding.

2. Energy of bond is $\propto$ overlap of atomic orbitals, and stabilization of non-bonding elements (lone pairs).

3. Hybridize orbitals to gain more favorable spatial/geometric arrangement of electrons.

4. Hybridization comes at the expense of promoting lower energy electrons to higher levels (to allow those orbitals to participate in bonding).

5. Hybridization scheme is favorable when overlap and lone pair repulsion outweigh energy cost of promotion.

6. Semi-quantitative / Empirical Approach.

(a) Describe relative magnitudes of atomic orbital energy levels,

(b) Pictorial views of overlap / lone pair stabilization.

(c) Use empirical structure measurements to gain understanding of physical mechanism of that structure, (particularly for molecules which deviate from perfect geometries). Mainly hybridization & % orbital contributions

↳ insights inform computational chemistry for predictive power.

7. With hybridization, % orbital contributions:

↳ determine: bond enthalpies / strength

↳ spectroscopy,

↳ reactivity / stability

↳ most probable structures (empirical formulae). (C_6H_6 → isoforms of benzene)

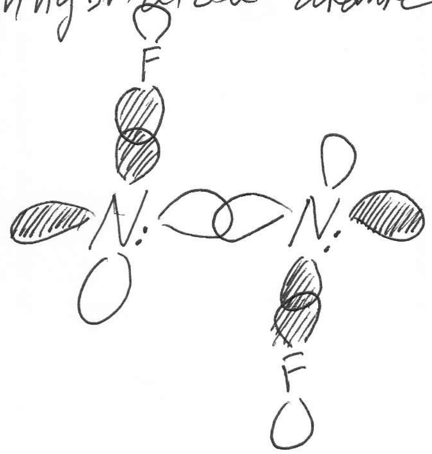
→ will most likely wait until MO theory to do this.

→ Beauty of VBT lies in intuitive nature, quick, generally reliable 1st order approximation of bonding.

Example: N_2F_2

By Lewis Diagram:

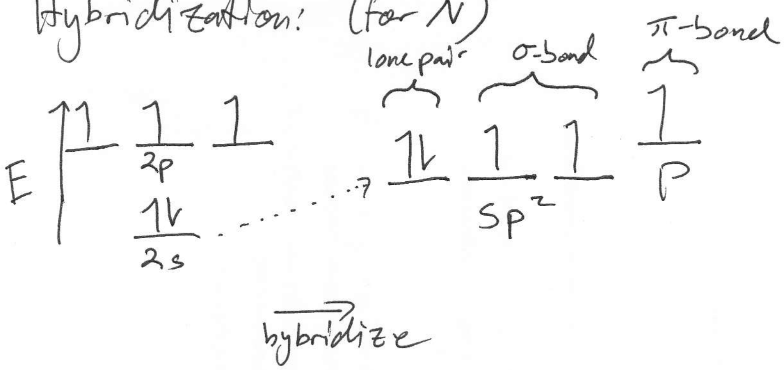
w/ unhybridized atomic orbitals:



↦ either poor overlap between bonding orbitals (2s-orbital buried).

↦ or lone pair instability (distributed across remaining 2p orbital or buried in 2s).

Hybridization: (for N)



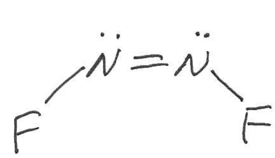
· Energy required to promote 2s e^- to sp^2 ≤ energy gained from better overlap/ lone pair stabilization.

From qualitative VBT/VSEPR:

$\angle_{N\text{-}N\text{-}F} \sim 120°$

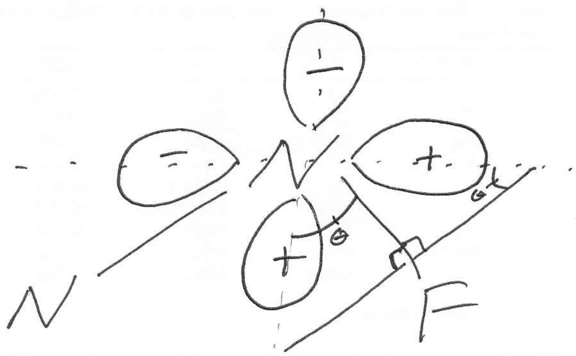
But more accurately:

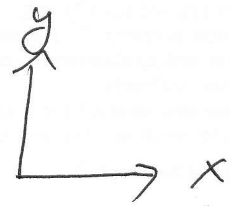
$\angle_{N\text{-}N\text{-}F} = 114.15°$



↦ what is physical reasoning behind deviation from ideal geometry? How does this insight help us predict future molecules?

Forming empirical hybrid orbitals:





$\theta = \frac{114.15°}{2}$

assume $2p_z$ only contributes to π-bond

↳ form hybrid orbitals from $2s, 2p_x, 2p_y \rightarrow \varphi_{N-F}, \varphi_{N-N}, \varphi_{l.p.}$

(3 a.o.'s must give 3 hybrid orbitals).

$$\varphi_{N-F} = c_1 2s + N_1 \cos\theta\, 2p_y + N_1 \sin\theta\, 2p_x$$

$$\varphi_{N-N} = c_2 2s + N_2 \cos\theta\, 2p_y - N_2 \sin\theta\, 2p_x$$

$$\varphi_{l.p.} = c_3 2s + c_4 2p_y + c_5 2p_x$$

Apply orthogonality condition! (hint. a.o.'s start out orthonormal).

$$\int \varphi_{N-F}\varphi_{N-N}\, d\tau = c_1 c_2 + N_1 N_2 \cos^2\theta - N_1 N_2 \sin^2\theta = 0$$

$$c_1 c_2 + N_1 N_2 \cos 2\theta = 0 \qquad (a)$$

$$\int \varphi_{N-F}\varphi_{l.p.}\, d\tau = c_1 c_3 + c_4 N_1 \cos\theta + c_5 N_1 \sin\theta = 0 \qquad (b)$$

$$\int \varphi_{N-N}\varphi_{l.p.}\, d\tau = c_2 c_3 + c_4 N_2 \cos\theta - c_5 N_2 \sin\theta = 0 \qquad (c)$$

Apply normality condition:

$$\int \varphi_{N\text{-}F}^2 \, d\tau = C_1^2 + N_1^2 \cos^2\theta + N_1^2 \sin^2\theta = 1$$

$$C_1^2 + N_1^2 [\cos^2\theta + \sin^2\theta] = 1$$

$$C_1^2 + N_1^2 = 1 \qquad (d)$$

$$\int \varphi_{N\text{-}N}^2 \, d\tau = C_2^2 + N_2^2 \cos^2\theta + N_2^2 \sin^2\theta = 1$$

$$C_2^2 + N_2^2 = 1 \qquad (e)$$

$$\int \varphi_{l.p.}^2 \, d\tau = C_3^2 + C_4^2 + C_5^2 = 1 \qquad (f)$$

Total
Unit orbital contribution from each hybrid orbital must $= 1$ for given a.o.

$$\int 2s(\varphi_{N\text{-}F} + \varphi_{N\text{-}N} + \varphi_{l.p.}) d\tau = C_1^2 + C_2^2 + C_3^2 = 1 \qquad (g)$$

$$\int 2p_{\cancel{y}}(\varphi_{N\text{-}F} + \varphi_{N\text{-}N} + \varphi_{l.p.}) d\tau = N_1^2 \cos^2\theta + N_2^2 \cos^2\theta + C_4^2 = 1$$

$$\int 2p_{\cancel{x}}(\varphi_{N\text{-}F} + \varphi_{N\text{-}N} + \varphi_{l.p.}) d\tau = N_1^2 \sin^2\theta + N_2^2 \sin^2\theta + C_5^2 = 1$$

→ not unique equations, can be obtained from other relations.

System of Equations

(a) $C_1 C_2 + N_1 N_2 \cos 2\theta = 0$

(b) $C_1 C_3 + C_4 N_1 \cos\theta + C_5 N_1 \sin\theta = 0$

(c) $C_2 C_3 + C_4 N_2 \cos\theta \ \cancel{+}\ C_5 N_2 \sin\theta = 0$

(d) $C_1^2 + N_1^2 = 1$

(e) $C_2^2 + N_2^2 = 1$

(f) $C_3^2 + C_4^2 + C_5^2 = 1$

(g) $C_1^2 + C_2^2 + C_3^2 = 1$

7 unknowns $\{C_1, C_2, C_3, C_4, C_5, N_1, N_2\}$

↓

7 unique equations

↓

$\emptyset$ degrees of freedom.

↓

difficult, but solvable.

Solve for 2 variables, determine solution graphically:

1) Combine (a), (d), (e) to eliminate c_1, c_2.

(d) $c_1^2 + n_1^2 = 1 \rightarrow c_1 = (1-n_1^2)^{1/2}$

(e) $\rightarrow c_2 = (1-n_2^2)^{1/2}$

(a) $\left[(1-n_1^2)(1-n_2^2)\right]^{1/2} + n_1 n_2 \cos 2\theta = 0$

2) solve for c_3, combine and equate.

(f) $c_3^2 + c_4^2 + c_5^2 = 1 \rightarrow c_3^2 = 1 - c_4^2 - c_5^2$

(3) $c_1 c_3 + c_4 n_1 \cos\theta + c_5 n_1 \sin\theta = 0$

$$c_3^2 = \frac{1}{c_1^2}\left[c_4 n_1 \cos\theta + c_5 n_1 \sin\theta\right]^2$$

sub in for c_1; rearrange

from (5)

$$c_3^2 = \frac{n_1^2}{1-n_1^2}(c_4\cos\theta + c_5\sin\theta)^2 = 1 - c_4^2 - c_5^2$$

solve for n_1^2: $$\frac{1}{\frac{1}{n_1^2}-1} = \frac{1-c_4^2-c_5^2}{(c_4\cos\theta + c_5\sin\theta)^2}$$

$$n_1^2 = \left[\left(\frac{1-c_4^2-c_5^2}{(c_4\cos\theta + c_5\sin\theta)^2}\right)^{-1} + 1\right]^{-1}$$

similarly:

$$n_2^2 = \left[\left(\frac{1-c_4^2-c_5^2}{(c_4\cos\theta - c_5\sin\theta)^2}\right)^{-1} + 1\right]^{-1}$$

3) Combine (f) and (g)

$$(f)\quad c_3^2 + c_4^2 + c_5^2 = 1 \rightsquigarrow c_3^2 = -c_4^2 - c_5^2 + 1$$

$$(g)\quad c_3^2 + c_1^2 + c_2^2 = 1 \rightsquigarrow c_3^2 = -c_1^2 - c_2^2 + 1$$

$$\hookrightarrow c_4^2 + c_5^2 - 1 = c_1^2 + c_2^2 - 1$$

$$= (1-N_1^2) + (1-N_2^2) - 1$$

$$c_4^2 + c_5^2 + N_1^2 + N_2^2 - 2 = 0$$

4) Solve reduced system of equations:

$$N_1^2 = \left[\left(\frac{1-c_4^2-c_5^2}{(c_4\cos\theta + c_5\sin\theta)^2}\right)^{-1} + 1\right]^{-1}$$

$$N_2^2 = \left[\left(\frac{1-c_4^2-c_5^2}{(c_4\cos\theta - c_5\sin\theta)^2}\right)^{-1} + 1\right]^{-1}$$

$$\left.\begin{aligned} &\left[(1-N_1^2)(1-N_2^2)\right]^{1/2} + N_1 N_2 \cos 2\theta = 0 \\ &c_4^2 + c_5^2 + N_1^2 + N_2^2 - 2 = 0 \end{aligned}\right\}$$

w/ test values for c_4, c_5, solve for N_1, N_2, plug into these two equations, iterate until both $= 0$.

From Excel (or whatever computational software)

Optimum values found for $c_4 \approx 0.52$, $c_5 \approx 0.55$

* note: coefficients may be off by ±5% due to complexity of numerical calculation.

Solving back for the other coefficients:

$$\varphi_{N-F} \approx 0.75\,2s + 0.36\,2p_y + 0.55\,2p_x$$

$$\varphi_{N-N} \approx 0.28\,2s + 0.52\,2p_y - 0.81\,2p_x$$

$$\varphi_{l.p.} \approx 0.65\,2s + 0.52\,2p_y + 0.55\,2p_x$$

	2s	2p
φ_{N-F}	~56%	~43%
φ_{N-N}	~8%	~92%
$\varphi_{l.p.}$	~42%	~57%

* Caveat: unit orbital contributions for $2p_x$ and $2p_y$ alone do not quite add up, largely due to errors in the iterative calculation. For most problems for this course, the algebra will be significantly more analytical.