SOLUTIONS

PROBLEM SET 8

CHM 3411, Dr. Chatfield

1. In these answers, I will write unnormalized wavefunctions. They can be normalized if needed.

(a) $\underline{\Psi}(1,2) = \psi_{H1s}(1)\, \psi_{F2p_z}(2) + \psi_{H1s}(2)\, \psi_{F2p_z}(1)$

(b) Define $\underline{\Psi}_{HF}$ as the wavefunction above

Define $\underline{\Psi}_{H^+F^-} = \psi_{F2p_z}(1)\, \psi_{F2p_z}(2)$
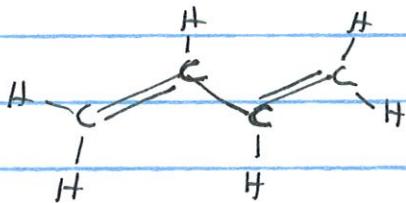
$\underline{\Psi} = \underline{\Psi}_{HF} + \lambda\, \underline{\Psi}_{H^+F^-}$

(c) Define $\underline{\Psi}_{H^-F^+} = \psi_{H1s}(1)\, \psi_{H1s}(2)$

$\underline{\Psi} = \underline{\Psi}_{HF} + \lambda_1\, \underline{\Psi}_{H^+F^-} + \lambda_2\, \underline{\Psi}_{H^-F^+}$

Chemical intuition tells us that the $\underline{\Psi}_{H^+F^-}$ term will be more important than the $\underline{\Psi}_{H^-F^+}$ term because F has larger electronegativity than H. Therefore we expect $\lambda_1 > \lambda_2$.

2. The Kekule structure is:

- Each C is sp² hybridized
- There are 6 C-H σ bonds, each formed from a C sp² hybrid orbital and an H1S orbital:

$$\psi_{\sigma CH} = \psi_{H1S}(1)\,\psi_{Csp^2}(2) + \psi_{H1S}(2)\,\psi_{Csp^2}(1)$$

- There are 2 C-C σ bonds, each formed from 2 sp² hybrid orbitals:

$$\psi_{\sigma CC} = \psi_{sp^2 A}(1)\,\psi_{sp^2 B}(2) + \psi_{sp^2 A}(2)\,\psi_{sp^2 B}(1)$$

- There are 2 C-C π bonds, each formed from 2 p orbitals. It is arbitrary whether we call them p_x or p_y

$$\psi_\pi = \psi_{p_x A}(1)\,\psi_{p_x B}(2) + \psi_{p_x A}(2)\,\psi_{p_x B}(1)$$

3. (a) $h_1 = N(s + 2^{1/2} p)$

$$1 = \int h_1^* h_1 \, d\tau = N^2 \left[\int s^* s \, d\tau + 2 \int p^* p \, d\tau + 2^{1/2} \int s^* p \, d\tau \right.$$

$$\left. + 2^{1/2} \int p^* s \, d\tau \right] = 3N^2$$

$$N = 3^{-1/2}$$

(b) $h_3 = N(s - p_x + p_y - p_z)$
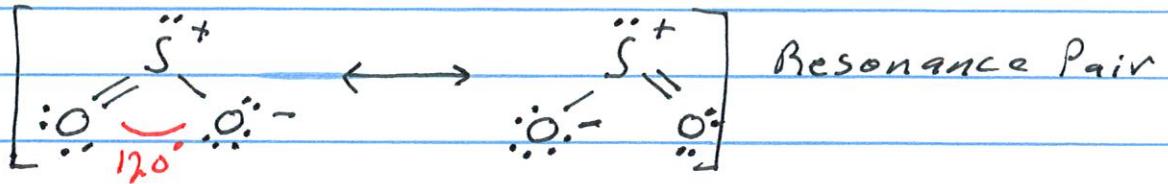
$$1 = N^2 \left[\int s^* s \, d\tau + \int p_x^* p_x \, d\tau + \int p_y^* p_y \, d\tau + \int p_z^* p_z \, d\tau \right.$$

$$- \int s^* p_x \, d\tau + \dots \text{ (all the other combinations}$$

are of orthogonal orbitals,

so each integral is 0)
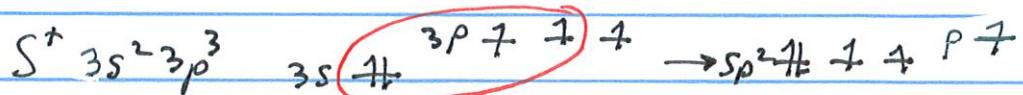
$$= 4N^2$$

$$N = \frac{1}{2}$$

4. SO_2 Lewis structures
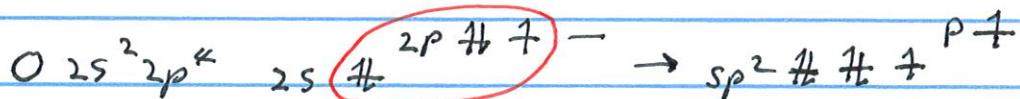
Resonance Pair

Valence bond description (also resonance pair):

S^+ $3s^2 3p^3$ $3s$ (⇅) $\overset{3p}{↑ \; ↑ \; ↑}$ → sp^2 ⇅ ↑ ↑ $\overset{p}{↑}$

    2 half-filled sp^2 orb. for σ bonds
    1 filled .. .. .. lone pair
    1 half-filled p .. .. Π bond

O $2s^2 2p^4$ $2s$ (⇅) $\overset{2p}{⇅ \; ↑ \; -}$ → sp^2 ⇅ ⇅ ↑ $\overset{p}{↑}$
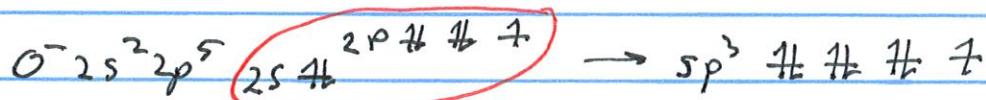
    1 half-filled sp^2 orb. for σ bond
    2 filled .. .. .. lone pairs
    1 half-filled p .. .. Π bond

O^- $2s^2 2p^5$ $2s$ ⇅ $\overset{2p}{⇅ \; ⇅ \; ↑}$ → sp^3 ⇅ ⇅ ⇅ ↑
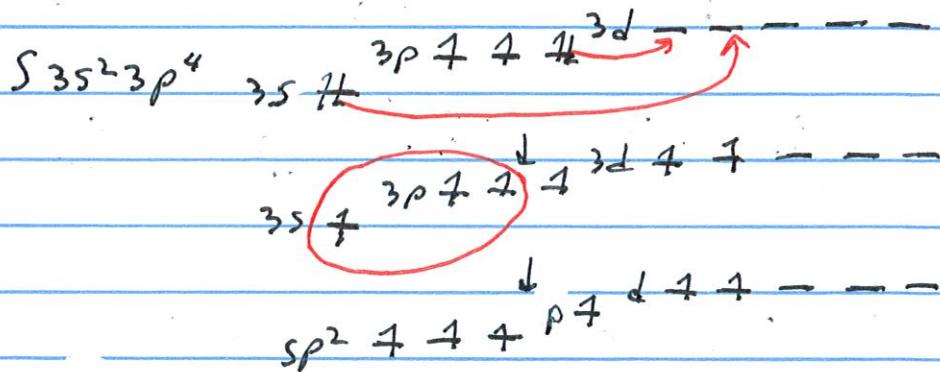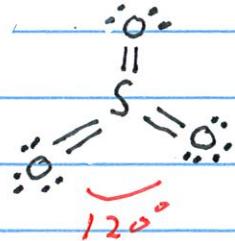
    1 half-filled sp^3 orb. for σ bond
    3 filled .. .. .. lone pairs
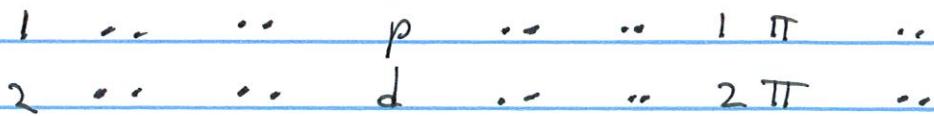
Description fits either member of resonance pair

2) Expanded octet

Lewis structure of SO_3 with $120°$ angle marked

$S\ 3s^2 3p^4$

Orbital diagrams for S showing $3s$, $3p$, $3d$ promotion and sp^2 hybridization
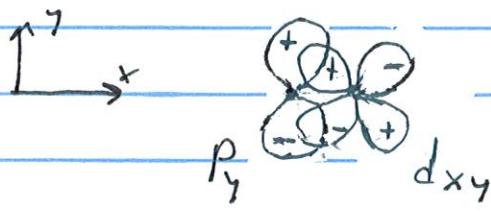
3 half-filled sp^2 orb. for 3 σ bonds

| 1 | .. | .. | p | .. | .. | 1 π | .. |
| 2 | .. | .. | d | .. | .. | 2 π | .. |

It may surprise you, but the proper d + p orbitals can overlap favorably to form a π bond:

P_y d_{xy}

- Favorable overlap (constructive
- Nodal plane   interference)
  through internuclear axis

The orientation of the 2 d orb. for forming these π bonds is not ideal in SO_3, but it is favorable enough.

5. Assume 2s 2p_x 2p_y for simplicity

Table 9A.1   Table 8C.1 $g \propto r$

$$2s = R_{2,0}(g)\, Y_{0,0}(\theta,\phi) = \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(2-g)\, e^{-g/2}\left(\frac{1}{4\pi}\right)^{1/2} = A(g)$$

$n \quad l \quad l \quad m_l$

$$2p_x = R_{2,1}\left[\frac{1}{\sqrt{2}}(Y_{1,1} - Y_{1,-1})\right] = \frac{-1}{24^{1/2}}\left(\frac{Z}{A}\right)^{3/2} g\, e^{-g/2}\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$$

$\underbrace{\qquad\qquad\qquad\qquad}_{B(g,\theta)}$

$$2p_y = R_{2,1}\left[\frac{1}{\sqrt{2}}(Y_{1,1} + Y_{1,-1})\right] = B(g,\theta)\sin\phi$$
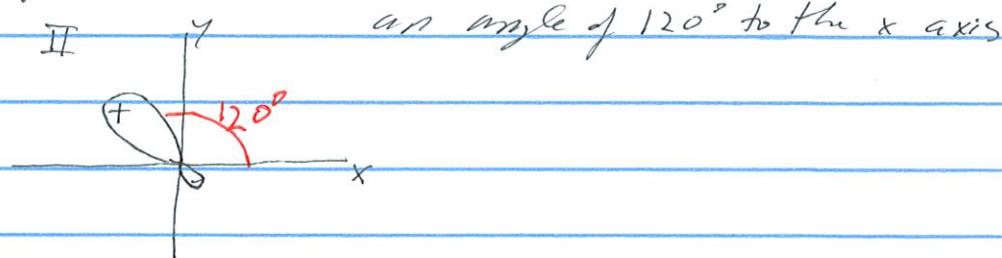
$$\psi = \frac{1}{\sqrt{3}}\left[A(g) - \frac{1}{\sqrt{2}}B(g,\theta)\cos\phi + \sqrt{\frac{3}{2}}\,B(g,\theta)\sin\phi\right]$$

We seek the angle ϕ for which ψ has a maximum.

$$\frac{d\psi}{d\phi} = 0 = \frac{B}{\sqrt{6}}\left[\sin\phi + \sqrt{3}\cos\phi\right]$$

$$\Rightarrow \tan\phi = -\sqrt{3} \qquad \phi = \tan^{-1}(-\sqrt{3}) = -60°$$

$\tan^{-1}$ has a periodicity of $180°$, so $-60°$ is equivalent to $120°$. Graphically, we know that the orbital must point in the direction of the 2nd quadrant. Therefore it makes an angle of $120°$ to the x axis

6. We assume ψ_A and ψ_B are normalized

$$1 = \int \psi^* \psi \, d\tau = N^2 \int (\psi_A + \lambda \psi_B)^* (\psi_A + \lambda \psi_B) \, d\tau$$

$$\psi = N(\psi_A + \lambda \psi_B)$$

$$= N^2 \left[\underbrace{\int \psi_A^* \psi_A \, d\tau}_{1} + \lambda^2 \underbrace{\int \psi_B^* \psi_B \, d\tau}_{1} + \lambda \underbrace{\int \psi_A^* \psi_B \, d\tau}_{S} \right.$$

$$\left. + \lambda \underbrace{\int \psi_B^* \psi_A \, d\tau}_{S} \right]$$

$$\frac{1}{N^2} = 1 + \lambda^2 + 2\lambda S$$

$$N = (\lambda^2 + 2\lambda S + 1)^{-1/2}$$