BF PROBLEM

\[ \text{BF} \quad \text{B} \quad \text{F} \]

\[ 2s^2 \quad 2p^1 \quad 2s^2 \quad 2p^5 \]

\[ \theta_1 \quad \theta_2 \quad \theta_3 \quad \theta_4 \]

\[ \pi_1 \quad \pi_2 \quad \pi_3 \quad \pi_4 \]

\[ \sigma_1 \quad \sigma_2 \quad \sigma_3 \quad \sigma_4 \]

** Orbitals: **

- \( \sigma_1 : 2s^2 \) (\( \pi_b \))
- \( \sigma_2 : 2s^2 + 2p^2 \) (\( \pi_a \))
- \( \sigma_3 : 2s^2 - 2p^2 \) (\( \pi_b \))
- \( \sigma_4 : 2p^2 \) (\( \pi_b \))

** \( \pi \) Orbitals: **

- \( 2 \times \pi_1 \) : \( 2p_{xy} + 2p_{xz} \)
- \( 2 \times \pi_2 \) : \( 2p_{xy} - 2p_{yz} \)

** Ordering:**

\( \sigma_1 < \sigma_2 < \pi_1 < \sigma_3 < \pi_2 < \sigma_4 \)

** Ground State Configuration:**

- B: \( 2s^2 \quad 2p^\uparrow \)
- F: \( 2s^2 \quad 2p^\uparrow \)

** G.S. Molecular Orbital Configuration:**

\( (\sigma_1)^2 \quad (\sigma_2)^2 \quad (\pi_1)^4 \quad (\sigma_3)^2 \)

** Diamagnetic**

** Why is the ordering incorrect? ** Experimentally, the ground state of BF is \( X^2^- \).

** Bond Order = 2 ** Does this make sense??

BF CO

- BF: Triple Bond
- CO: Triple Bond

- BF: LARGER \( \text{r}_e \)
- CO: Smaller \( \text{r}_e \)

0.120 \( \text{Å} \) 0.117 \( \text{Å} \)

0.705 eV 11.09 eV

\( \text{N} \) \( 1401 \text{ cm}^{-1} \) \( 2170 \text{ cm}^{-1} \)

\( \text{Consistent with } \text{BO} = 2 \)

** Corresponds to 1^{st} Order Cubature of Harmonic Approximation to Born-Oppenheimer Potential**
Energy of $\Delta_4$ vs $\Pi_2$

Lowest excited states of BF are $\alpha^3 \Pi$ and $\alpha' \Pi$

From $\Delta_3 \rightarrow \Pi_2$ transition

$\Pi_2 \quad \alpha_3 \quad \alpha_1 \quad \alpha_2$

If $\Delta_4$ were lower

$\Delta_4 \quad \alpha_3 \quad \alpha_1 \quad \alpha_2 \quad \rightarrow \Sigma^+$, $\Sigma^+$

Which is not correct

$\Rightarrow \Delta_4$ is somewhat antibonding (because it is larger in energy)

$\sigma_1$, $\sigma_2$, $\alpha_4$ are LCAO: $2s_B$, $2p_z B$, $2p_z F$

$\Delta_2 = a_2 \tau_2 s_B + b_2 \tau_2 p_z B + c_2 \tau_2 p_z F$

$\Delta_3 = \ldots$

$\Delta_4 = \ldots$

The fact that $\Delta_4$ is nonbonding is an oversimplification of what is going on.

MO bonding energies:

$N_2^+ (1s_A)^2 (1s_A)^2 (2s_A)^2 (2p_A)^2 (2p_\Pi)^4 (2p_\sigma)^2$

Binding energy $E : N_2 \rightarrow N_2^+ (2p_\sigma)^+$

or $N_2^+ (2s_A)^+$

$N_2^- (1s_A)^+$
PHOTOELECTRON SPECTROSCOPY DETERMINES BINDING ENERGIES

\[ h\nu \rightarrow [\cdot \cdot]^{\pm} + e^- \]

MEASURE KINETIC ENERGY (cKE) OF e-

\[ cKE = h\nu - E \]

\[ N_2^+ \]

\[ \text{N}_2 \]

\[ 2\sigma_g \]

\[ 2\pi \tau_u \]

\[ \ldots \]

\[ 2\pi \delta_g \]

\[ = 1\sigma_g \]

\[ 1\sigma_g \]

\[ \text{N}_2^+ \text{ FIG. 9-16} \]

Almost degenerate, but split a little due to spin orbit coupling

KEY POINTS: Big splitting between 2\sigma_g/\text{eV}

Much smaller for 1\sigma_g/\text{eV}

VALENCE vs. CORE ELECTRONS

MO are split by exchange interaction

Core electrons are localized near nuclei + splitting is similar to atomic core
IS ORBITAL EXPERIENCES FULL NUCLEAR CHARGE

\[ \epsilon_{1s}(Ne) > \epsilon_{1s}(F) > \epsilon_{1s}(N) > \epsilon_{1s}(O) \]  
VALUES INDEPENDENT OF MOLECULAR STRUCTURE

\[ \epsilon_{1s}(O) \sim 300eV \]