NH₃ MO Scheme

- The approach to NH₃ is similar to that for H₂O.

\[
\begin{array}{c}
\text{N} \\
\text{H} \quad \text{H} \\
\text{H}
\end{array}
\]

<table>
<thead>
<tr>
<th>(C_{3v})</th>
<th>(E)</th>
<th>(2C_3)</th>
<th>(3\sigma_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_{SALC})</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

\(\Gamma_{SALC} = A_1 + E\)

Nitrogen AO symmetries are

\[
s = A_1 \quad p_z = A_1 \quad (p_x, p_y) = E
\]
Matching AOs and SALCs

- All AOs match with SALCs, so there are no nonbonding levels.

- Both $s$ and $p_z$ AOs match the $A_1$ SALC, so $s$-$p$ mixing is likely.
  - If bonding and antibonding combinations were formed for both $s$ and $p_z$ AOs, we would end up with eight MOs, but only seven AOs on N and H are available (disregarding the $1s$ AO on N).
  - We must make only three MOs from the $s$ and $p_z$ AOs and the $A_1$ SALC.

- For simplicity, we will assume that the $s$ and $p_z$ AOs each form essentially separate bonding MOs, but that together they form a single mixed antibonding MO.
Qualitative MO Scheme for NH₃

\[
\begin{align*}
\sigma^*(s) a_1 \\
\sigma(x,y) e \\
\sigma(z) a_1 \\
\sigma^*(s-z) a_1 \\
\sigma^*(x,y) e \\
\sigma^*(s-z) a_1
\end{align*}
\]
P.E.S. of NH$_3$

- The P.E.S. has three bands with vibrational fine structure, indicative of ionizations from bonding MOs, consistent with the MO scheme above.

- The lowest energy ionization, corresponding to ejection of electrons from the $\sigma(z)\ a_1$ MO (the “lone pair” on NH$_3$), has pronounced fine structure, indicating its bonding character.$^1$

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MO and VB Models

- The VB model assumes one nonbonding lone pair in an $sp^3$ hybrid.

- As the MO scheme and P.E.S. data suggest, this pair is weakly bonding.

- This is not inconsistent with the well-known Lewis base character of NH$_3$, because the $\sigma(z)$ MO has considerable electron density above the nitrogen, not unlike the customary picture of the VB model's lone-pair $sp^3$ hybrid.

- A rough sketch of the MO is shown below: