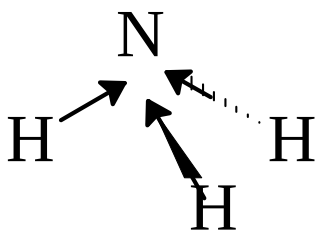
NH_3 MO Scheme

- The approach to NH_3 is similar to that for H_2O.



C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{SALC}	3	0	1

$$\Gamma_{SALC} = A_1 + E$$

Nitrogen AO symmetries are

$$s = A_1 \quad p_z = A_1 \quad (p_x, p_y) = E$$

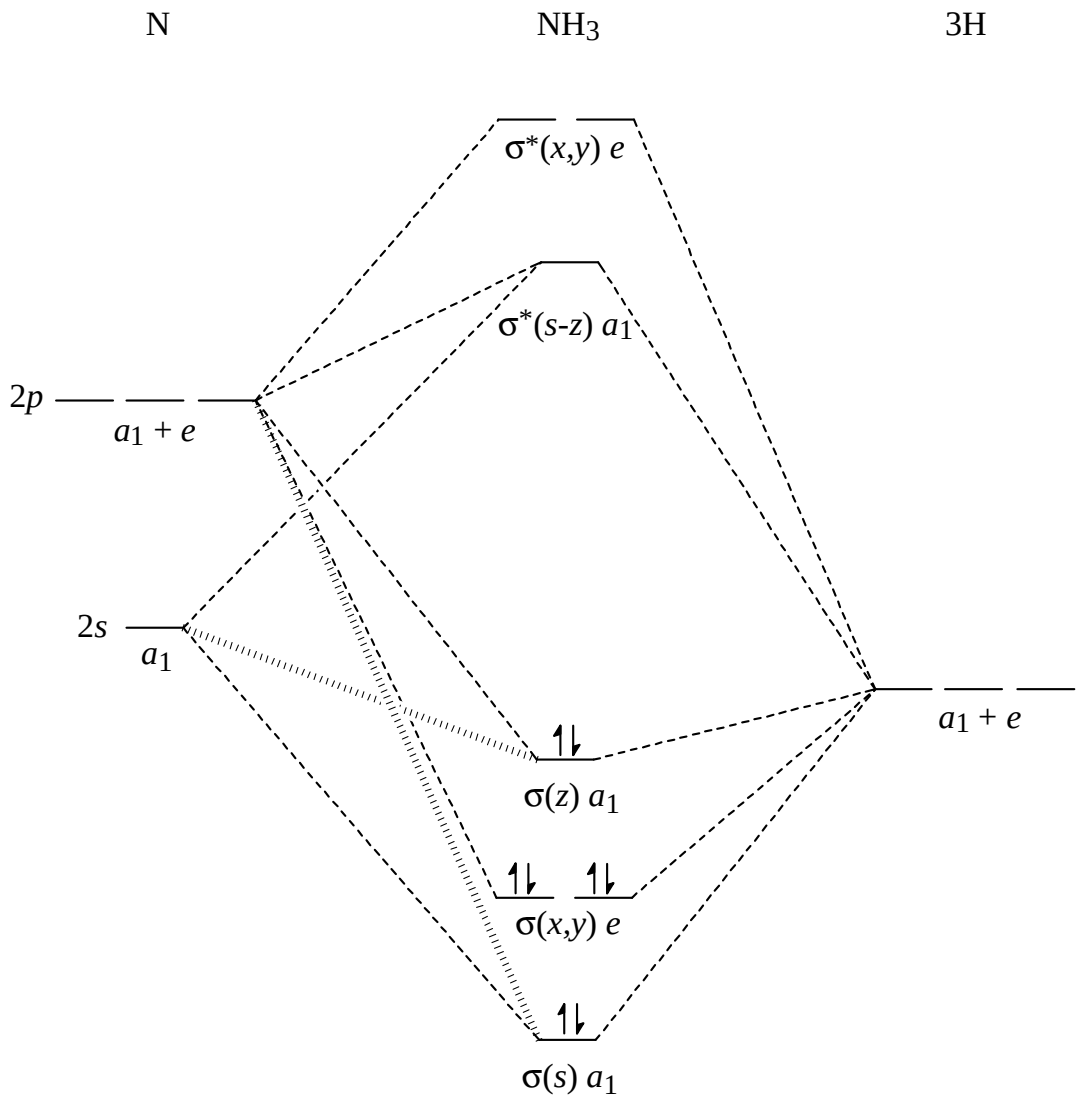
Matching AOs and SALCs

- 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 1*s* 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.

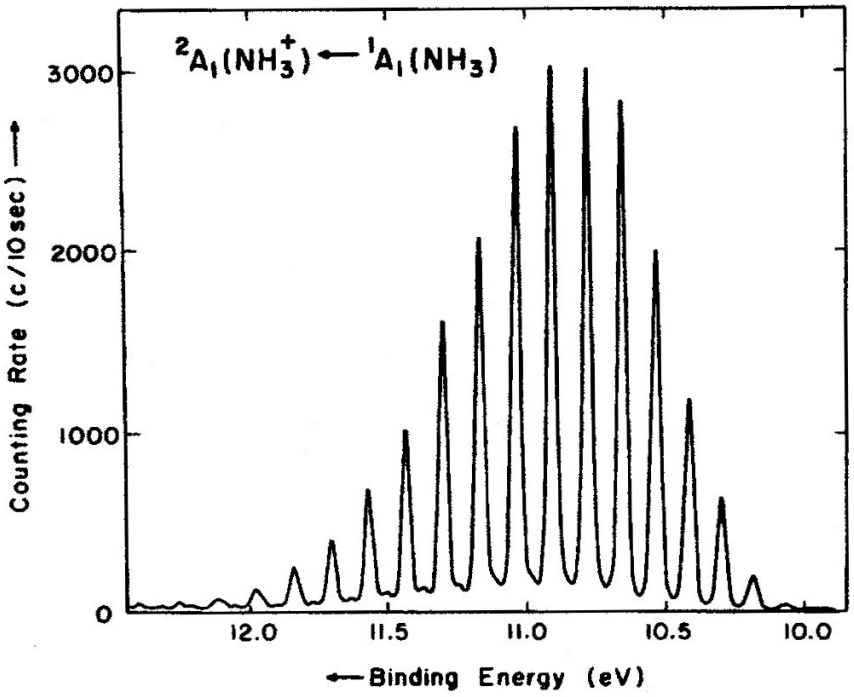
Qualitative MO Scheme for NH_3



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 σ(*z*) a_1 MO (the "lone pair" on NH_3), has pronounced fine structure, indicating its bonding character.[1]



[1] J. W. Rabalais, L. Karlsson, L. O. Werme, T. Bergmark, K. Siegbahn, *J. Chem. Phys.*, **1973**, *58*, 3370-3372; A. Peluso, R. Borrelli, A. Capobianco, *J. Phys. Chem A*, **2009**, *113*, 14831-14837.

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: