# Chem 241

## Lecture 8

# Recap

- Lewis Bases
- Hard and soft acid-base theory
- Symmetry E, $C_n$, $\sigma$ and i

# $S_n$, Improper rotation

- Rotation followed by a reflection in the perpendicular plane. ($C_n$ then $\sigma_h$)
- $S_2$ = i, $S_1 = \sigma$

# Flow chart

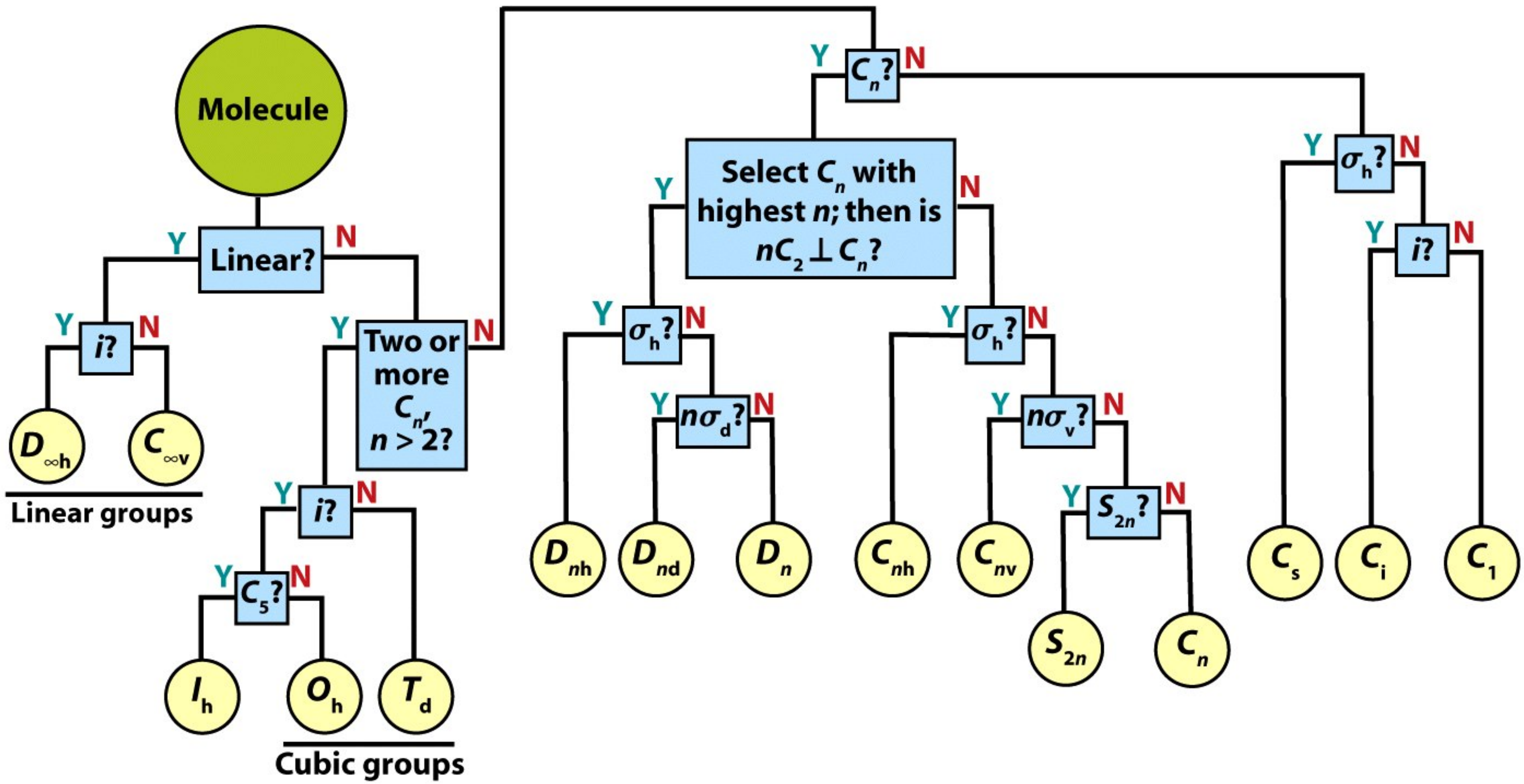


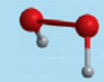
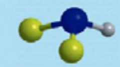
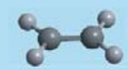
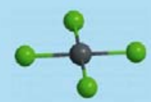

Figure 7-9
*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

# Practice

$NH_3$
$CO_2$
$[Fe_4S_4Cl_4]^{2-}$
$[Co(en)_3]^{3+}$ (ignore hydrogens)
Cyclohexane (conformation) chair
$[Fe(H_2O)_6]^{3+}$
Diborane

# Symmetry

**Table 7.2** The composition of some common groups

| Point group | Symmetry elements | Shape | Examples |
|---|---|---|---|
| $C_1$ | $E$ |  | SiClBrF |
| $C_2$ | $E, C_2$ |  | $H_2O_2$ |
| $C_s$ | $E, \sigma$ |  | $NHF_2$ |
| $C_{2v}$ | $E, C_2, \sigma_v, \sigma_v'$ |  | $H_2O$, $SO_2Cl_2$ |
| $C_{3v}$ | $E, 2C_3, 3\sigma_v$ |  | $NH_3$, $PCl_3$, $POCl_3$ |
| $C_{\infty v}$ | $E, C_2, 2C_\phi, \infty\sigma_v$ |  | CO, HCl, OCS |
| $D_{2h}$ | $E, 3C_2, i, 3\sigma$ |  | $N_2O_4$, $B_2H_6$ |
| $D_{3h}$ | $E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v$ |  | $BF_3$, $PCl_5$ |
| $D_{4h}$ | $E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d$ |  | $XeF_4$, *trans*-$[MA_4B_2]$ |
| $D_{\infty h}$ | $E, 2\infty C_2', 2C_\phi, i, \infty\sigma_v, 2S_\phi$ |  | $H_2$, $CO_2$, $C_2H_2$ |
| $T_d$ | $E, 8C_3, 3C_2, 6S_4, 6\sigma_d$ |  | $CH_4$, $SiCl_4$ |
| $O_h$ | $E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$ |  | $SF_6$ |

# Applications

- Molecular Properties.
  - a. Polarity
    - i. a molecule cannot be polar if it has an inversion center.
    - ii. A molecule cannot have an electric dipole moment perpendicular to any mirror plane.
    - iii. A molecule cannot have an electric dipole moment perpendicular to any axis of rotation.
  - b. Chirality
    - i. a molecule cannot be chiral if it has an $S_n$ axis

# Character Table

**Table 7.3** The components of a character table

| Name of point group* | Symmetry operations $R$ arranged by class ($E$, $C_n$, etc.) | Functions | Further functions | Order of group, $h$ |
|---|---|---|---|---|
| Symmetry species (Γ) | Characters ($\chi$) | Translations and components of dipole moments ($x$, $y$, $z$), of relevance to IR activity<br>Rotations (about axes $x$, $y$, $z$) | Quadratic functions such as $z^2$, $xy$, etc., of relevance to Raman activity | |

* Schoenflies symbol.

**Table 7.4** The $C_{2v}$ character table

| $C_{2v}$ | $E$ | $C_2$ | $\sigma(zx)$ | $\sigma'(yz)$ | $h = 4$ | |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | $z$ | $x^2$, $y^2$, $z^2$ |
| $A_2$ | 1 | 1 | −1 | −1 | $R_z$ | $xy$ |
| $B_1$ | 1 | −1 | 1 | −1 | $x$, $R_y$ | $xz$ |
| $B_2$ | 1 | −1 | −1 | 1 | $y$, $R_x$ | $yx$ |

# MO polyatomic

Consider $H_2O$

a. Point group = $C_{2v}$

b. 2 1s orbitals on equivalent H atoms generate 2 SALCs

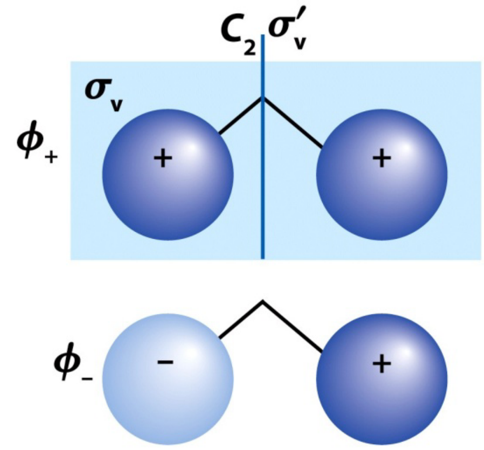
$\psi_1 = 1s\ (H_a) + 1s\ (H_b)$

$\psi_2 = 1s\ (H_a) - 1s\ (H_b)$

c. What symmetries do these SALCs have? (perform symmetry ops for the group, assign "1" if unchanged, "-1" if inverted.)

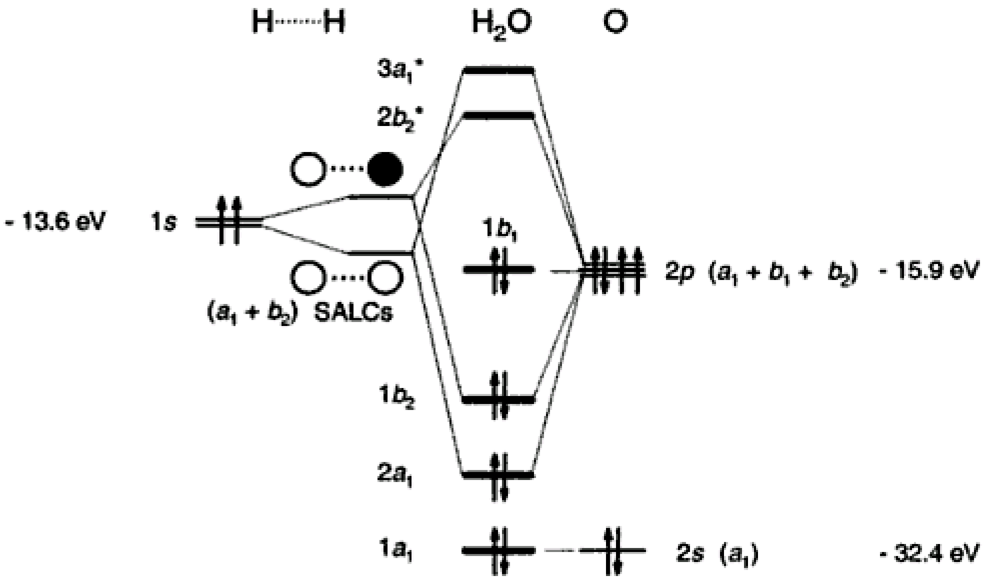
Can look up O AO symmetries (s, $p_z$–$A_1$; $p_x$–$B_1$; $p_y$–$B_2$)

d. Combine SALCS of the same symmetry



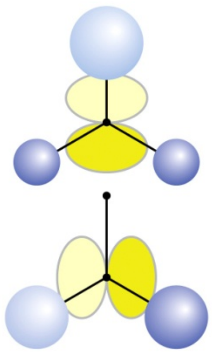
# Symmetry

- MO diagram for $H_2O$

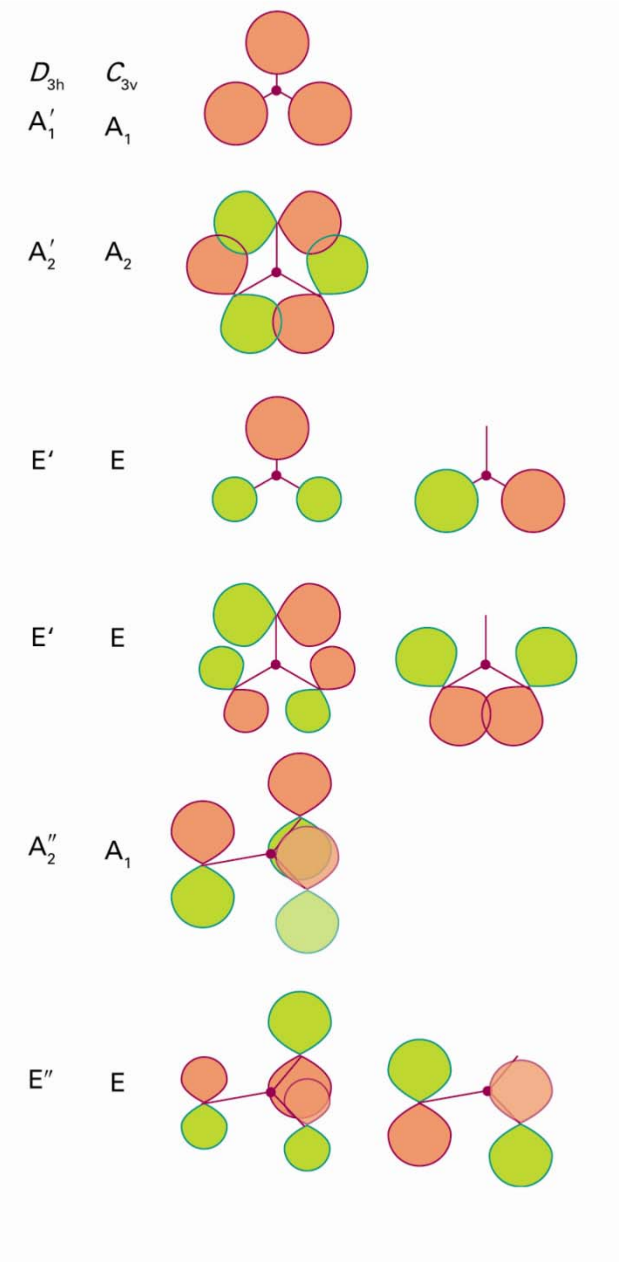


# A little more complex

- Consider $NH_3$
  a. Point group = $C_{3v}$
  b. 3 1s orbitals on equivalent H atoms generate 3 SALCs
     $\phi_1 = 1s\ (H_a) + 1s\ (H_b) + 1s\ (H_c)$ ---–$A_1$
     $\phi_2 = 2\ 1s\ (H_a) - 1s\ (H_b) – 1s\ (H_c)$ ----E
     $\phi_3 =\ 1s\ (H_b) – 1s\ (H_c)$ ----E
  c. What symmetries do these SALCs have? (perform symmetry ops for the group, assign "1" if unchanged, "-1" if inverted.
     Can look up O AO symmetries (s, $p_z$–$A_1$; $p_x$– E; $p_y$–E)
  d. Combine SALCS of the same symmetry



# A little more complex

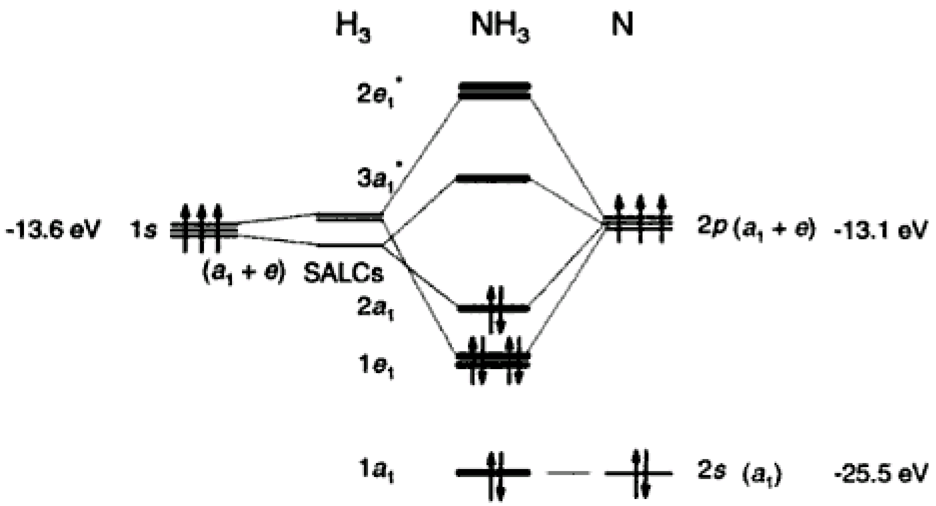


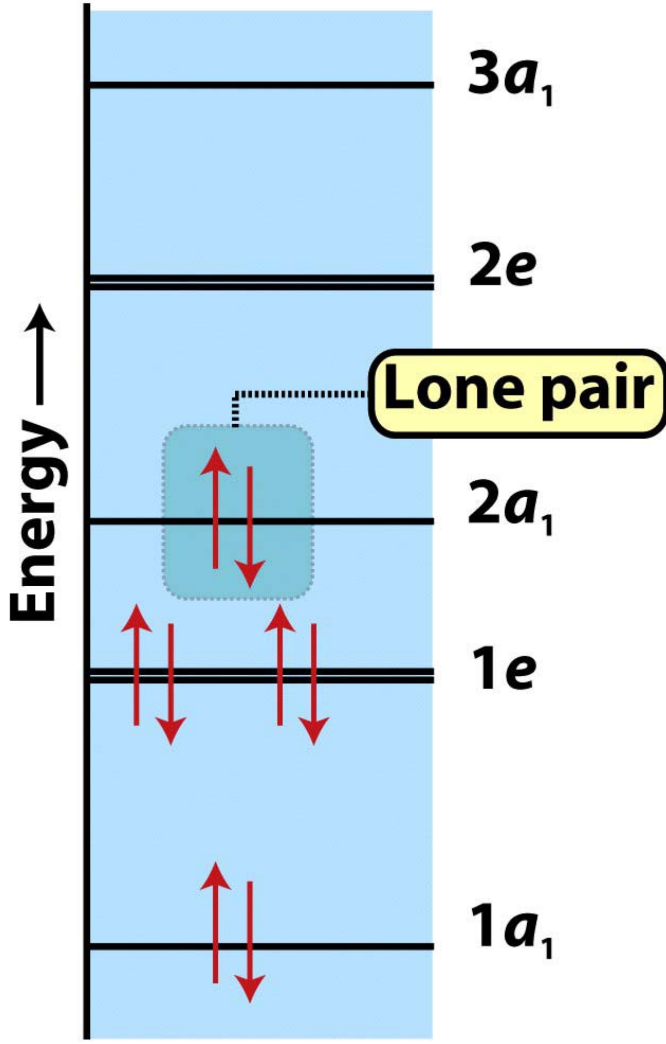
# Symmetry

- MO diagram for $NH_3$

**Table 7.5** The $C_{3v}$ character table

| $C_{3v}$ | $E$ | $2C_3$ | $3\sigma_v$ | $h=6$ | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | $z$ | $z^2$ |
| $A_2$ | 1 | 1 | −1 | $R_z$ | |
| E | 2 | −1 | 0 | $(x,y)$ $(R_x, R_y)$ | $(zx, yz)$ $(x^2-y^2, xy)$ |



# MO diagrams for polyatomics

- ba. Assign the molecule to a point group
- b. use the character table of that point group to generate SALCs for equivalent atoms, or look them up (see resource section 4 in Shriver)
- c. arrange the SALCs for each fragment in order of increasing energy, given issues of whether they derive from s, p or d etc. orbitals, and then the number of nodes in the wavefunction.
- d. Combine SALCs of the same symmetry type from the two fragments (equivalent atoms and central atom). (Remember N AOs generate N SALCs, which generate N MOs.)
- e. Confirm, correct, and revise the qualitative energy order by experiment (*e.g.*, PES) or by carrying out a calculation.

# Homework

- Chapter 7

Exercises: 7.2, 7.3, 7.6

Problem: 7.1

We will stop our discussion of symmetry at spectroscopic applications (section 7.8).

Additional courses that advance this material include Chem 546 (Advanced Inorganic) and Chem 648 (Coordination Chemistry)