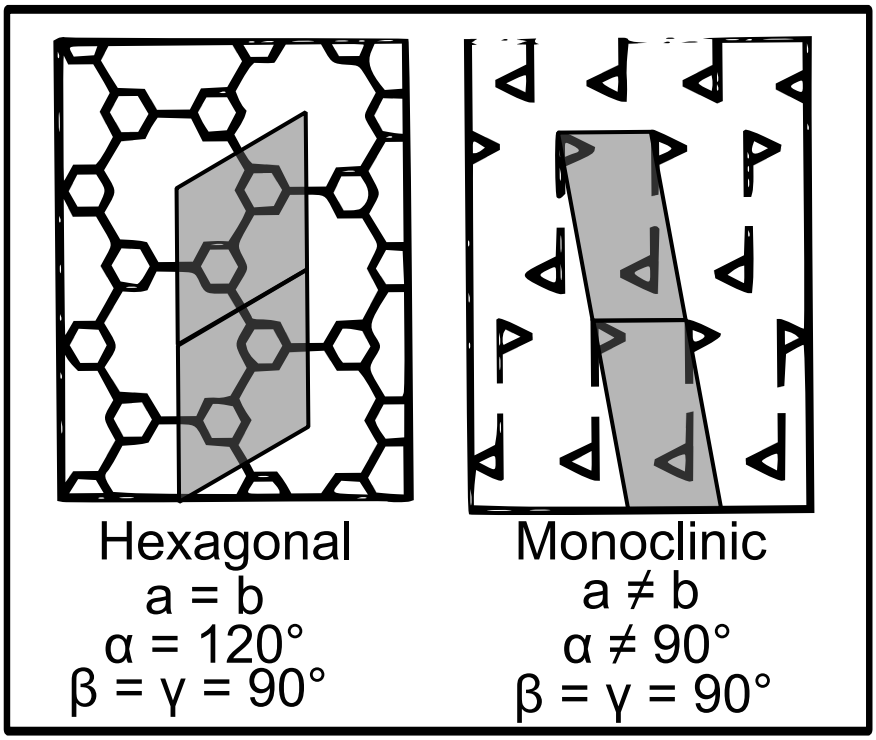
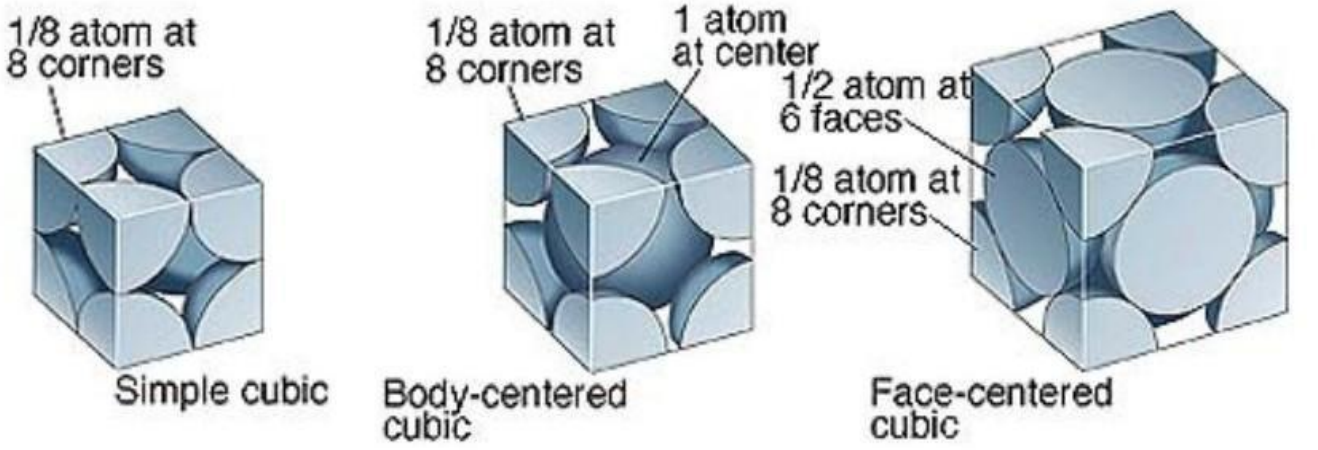
Exam 2 - Study Guide

Unit Cell



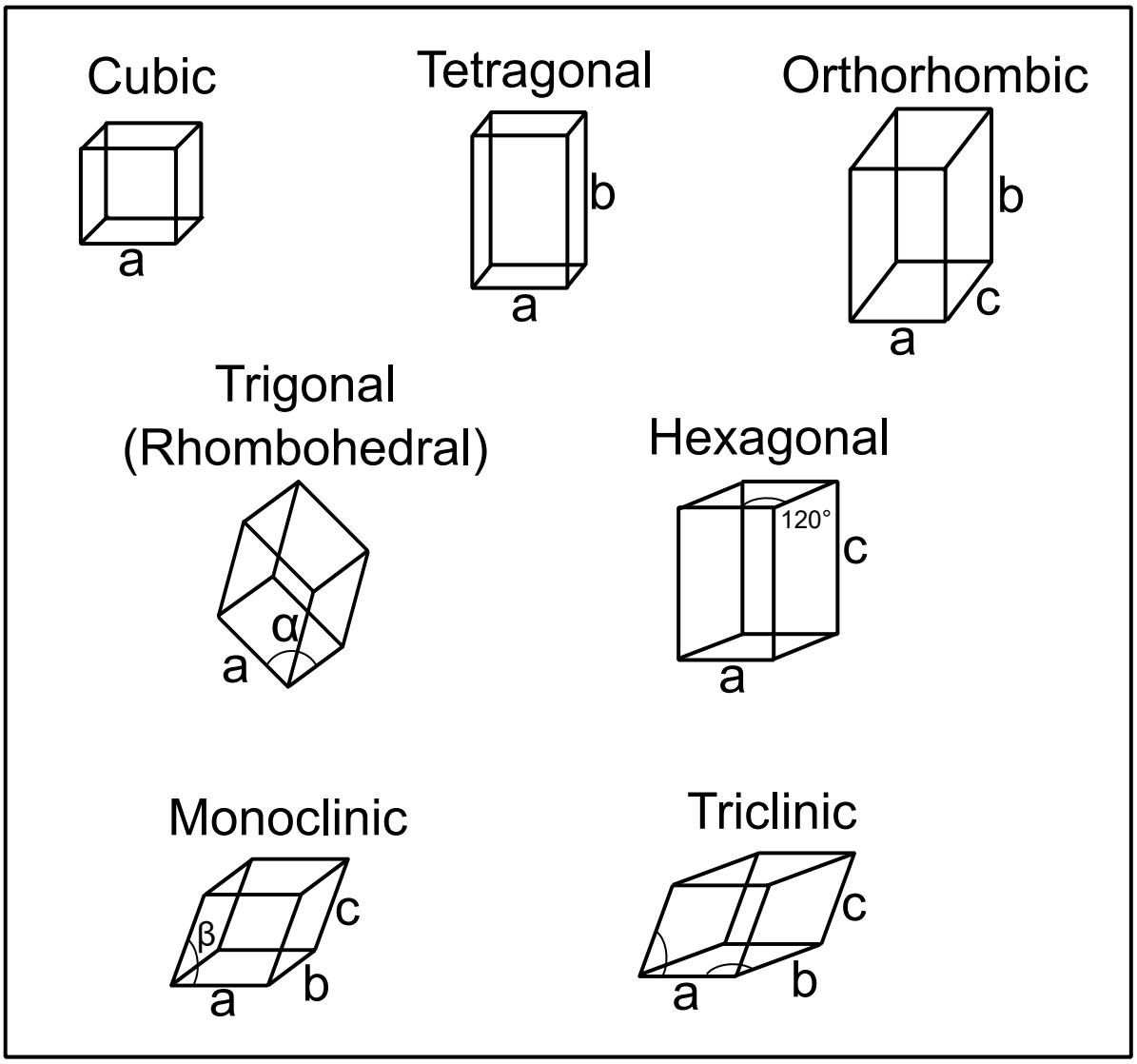


1. SC - Simple Cubic
    - 1 atom per unit cell
2. BCC - Body-Centered Cubic
    - 2 atoms per unit cell
3. FCC/CCP - Face-Centered Cubic / Cubic Close Packing
    - 4 atoms per unit cell

Crystal Systems

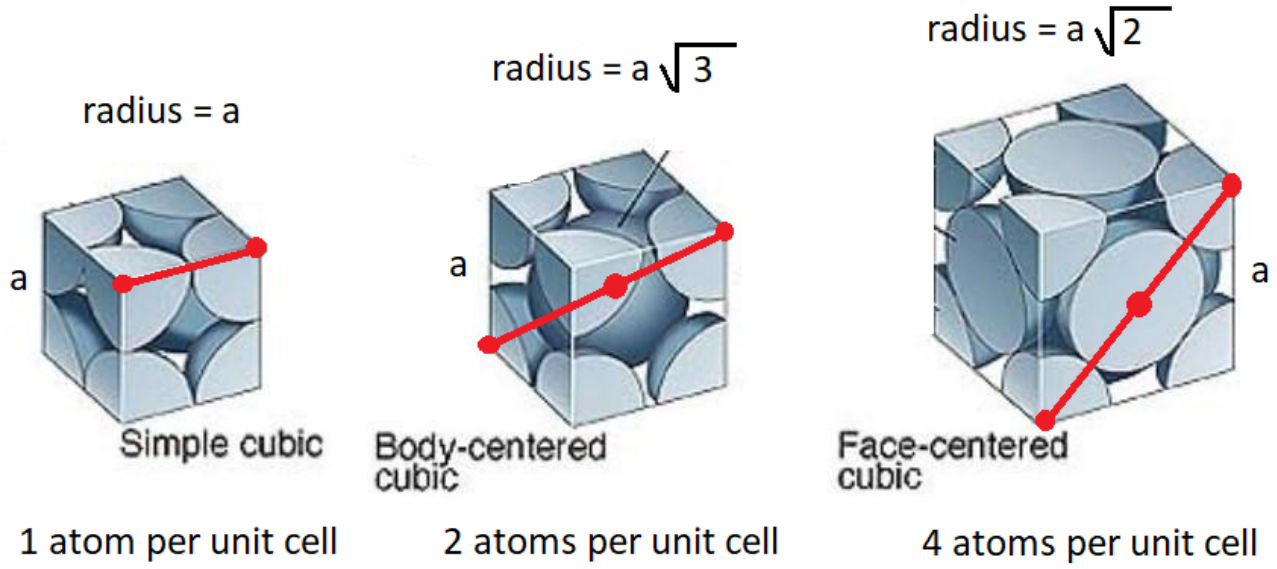
	Crystal System	Lattice dimensions	Arity	Required Parameters
1	Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$	1	a
2	Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$	2	a, c
3	Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	3	a, b, c
4	Trigonal (Rhombohedral)	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$	2	a, α
5	Hexagonal	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	2	a, c
6	Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$	4	a, b, c, β
7	Triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	6	a, b, c, α, β, γ

- If the question askes "if the third axis is perpendicular, what crystal system is drawn?", then the answer must be: cubic, tetragonal, orthorhombic, or hexagonal.
- Otherwise, the answer must be rhombohedra, monoclinic, or triclinic.


Cubic
a
Tetragonal
b
a
Orthorhombic
b
c
a
Trigonal
(Rhombohedral)
α
a
Hexagonal
120°
c
a
Monoclinic
β
c
a
b
Triclinic
c
a
b

Density and Radius

- Density is mass over volume
- Avogadro's number: 6.022×10^{23} atoms per mol
- 1 Å = 10^{-10} m
- An element will change density at different temperatures and pressures, causing the crystalline structure to change.
- The radius of a BCC is found by using the body-diagonal of the cube.
- The radius of the CCP is found by using the face-diagonal of the cube.



Example

At 20°C, Fe is bcc, with a side length of **a = 2.866 Å**.
At 950 °C, Fe is ccp, with a side length of **a = 3.43 Å**.

Steps for obtaining density:

1. Start with the atomic mass of Fe in grams per mol.
   Convert to grams per atom by using Avogadro's number.
2. Then to grams per unit cell by using the number of atoms per unit cell.
3. Then to grams per cubic angstrom, by using the cube of the value provided.
   At this point we've found density, but the value isn't in standard units.
4. Convert from cubic anstrom to cubic meters.
5. Convert from grams to kilograms.

Density @ 20°C

$$\frac{55.845\ \frac{g}{mol}}{6.022 \times 10^{23}\ \frac{atoms}{mol}} \times \frac{2\ \text{atoms}}{\text{BCC}} \times \frac{\text{BCC}}{(2.866\ \mathring{A})^3} \times \frac{\mathring{A}^3}{(10^{-10}\ m)^3} \times \frac{1\ kg}{1000\ g} = 7,879 kg/m^3$$

Density @ 950°C

$$\frac{55.845\ \frac{g}{mol}}{6.022 \times 10^{23}\ \frac{atoms}{mol}} \times \frac{4\ \text{atoms}}{\text{BCC}} \times \frac{\text{CCP}}{(3.43\ \mathring{A})^3} \times \frac{\mathring{A}^3}{(10^{-10}\ m)^3} \times \frac{1\ kg}{1000\ g} = 9,192 kg/m^3$$

Radius @ 20°C

- In a cube with a side of length a, its body diagonal has length $a\sqrt{3}$.
- There are 4 radii along the length of a body diagonal.

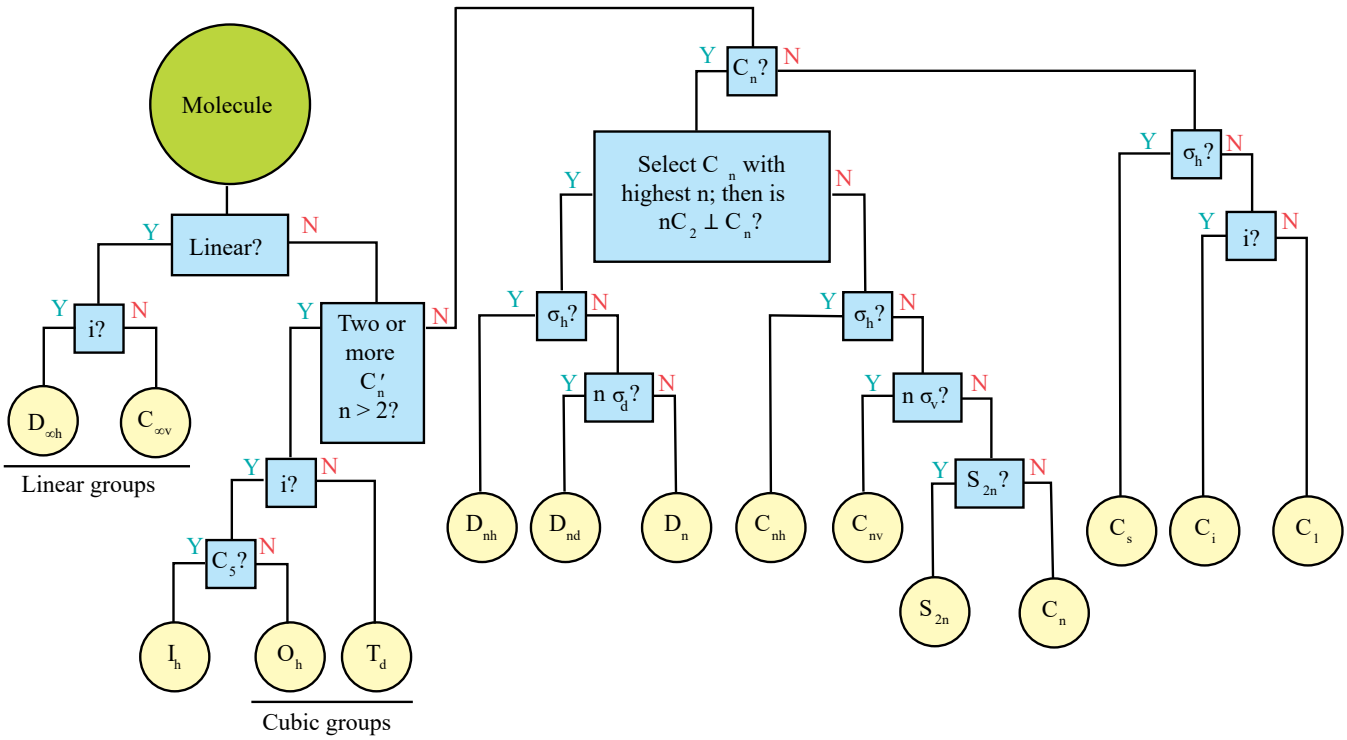
$$\frac{2.866\ \mathring{A} \times \sqrt{3}}{4\ \text{radii}} = 1.241\ \mathring{A}$$

Radius @ 950°C

- In a cube with a side of length a, its face diagonal has length $a\sqrt{2}$.
- There are 3 radii along the length of a face diagonal.

$$\frac{3.43\ \mathring{A} \times \sqrt{2}}{3\ \text{radii}} = 4.85\ \mathring{A}$$

Point Groups



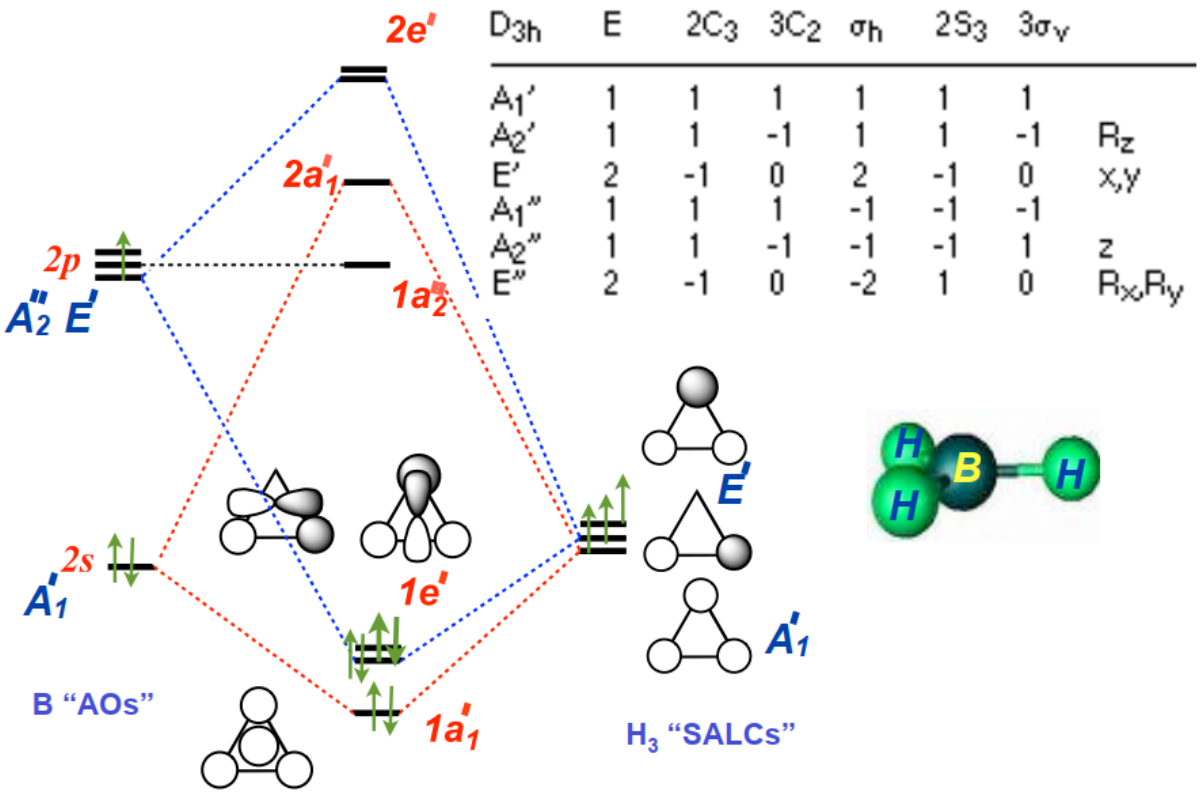
The decision tree for identifying a molecular point group. The symbols of each point refer to the symmetry elements.

1. Is the molecule linear?
   Yes: Is there a center of inversion?
   Yes: $D_{\infty h}$ (e.g. Carbon dioxide)
   No: $C_{\infty h}$ (e.g.) (Hydrogen chloride)
2. Are there two or more C'_n where n > 2?
   Yes: Is there a center of inversion?
   Yes: Does it have a C_5 element?
   Yes: I_h (e.g. Buckminsterfullerene)
   No: O_h (e.g. Sulfur Hexafluoride, Cubane)
   No: T_d (e.g. Methane)
3. Does C_n exist?
   No: Is there a horiztonal mirror plane (σ_h)?
   Yes: C_s
   No: Is there a center of inversion?
   Yes: C_i
   No: C_1
4. Select C_n with highest n, is there a C_2 axis perpendicular to that C_n?
   Yes: Is there a horiztonal mirror plane (σ_h)?
   Yes: D_{nh}
   No: Is there a dihedral mirror plane (σ_d)
   Yes: D_{nd}
   No: D_n
5. Is there a horiztonal mirror plane (σ_h)
   Yes: C_{nh}
6. Is there a vertical mirror plane (σ_v)?
   Yes: C_{nv}
7. Is it S_{2n}?
   Yes: S_{2n}
   No: C_n

MO Diagram

- HOMO - highest occupied molecular orbital
- LUMO - lowest unoccupied molecular orbital

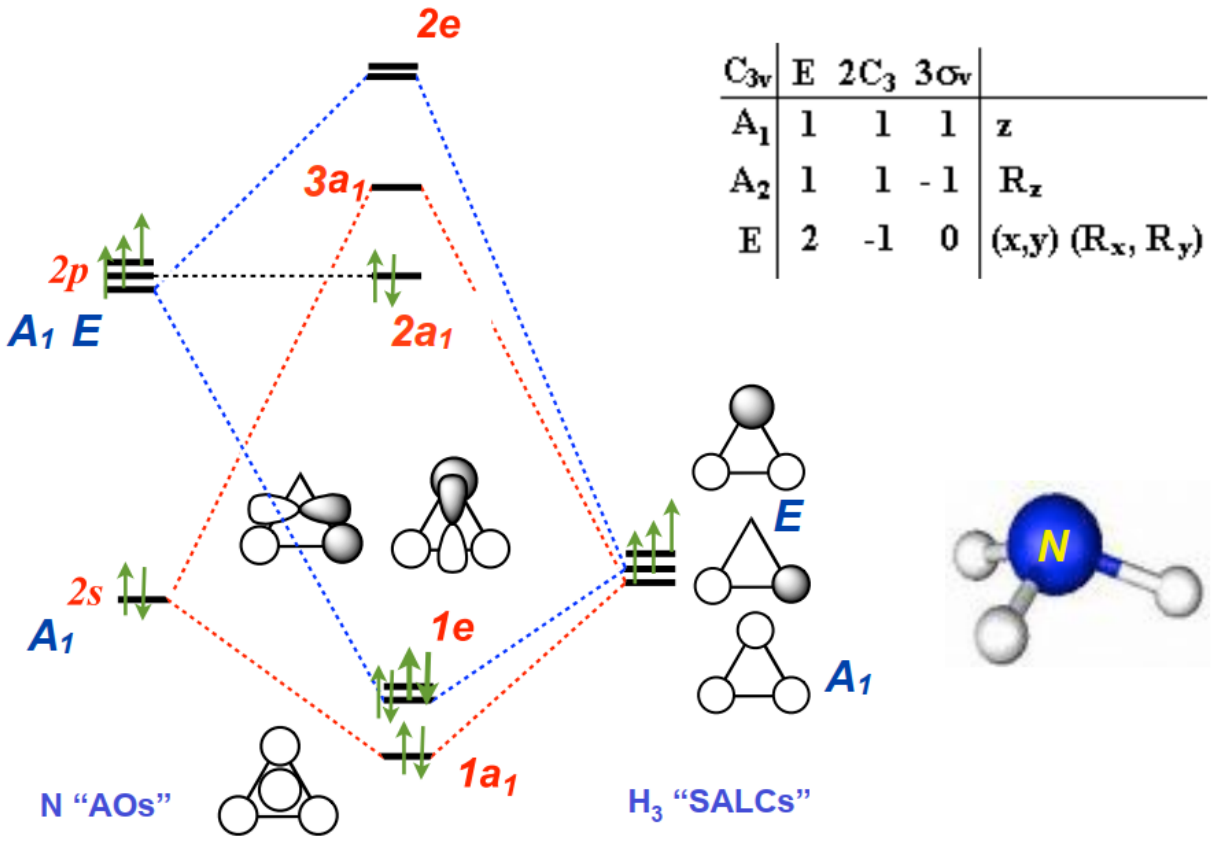
BH_3



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	R_z
E'	2	-1	0	2	-1	0	x,y
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	z
E''	2	-1	0	-2	1	0	R_x,R_y

BH_3 is an acid because it's LUMO is an unfilled bonding orbital with $1a''_2$ symmetry.

NH_3



C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y) (R_x, R_y)

NH_3 is a base because its HOMO is a filled bonding orbital with $2a_1$ symmetry, so it's more willing to donate electrons than it is to accept them.