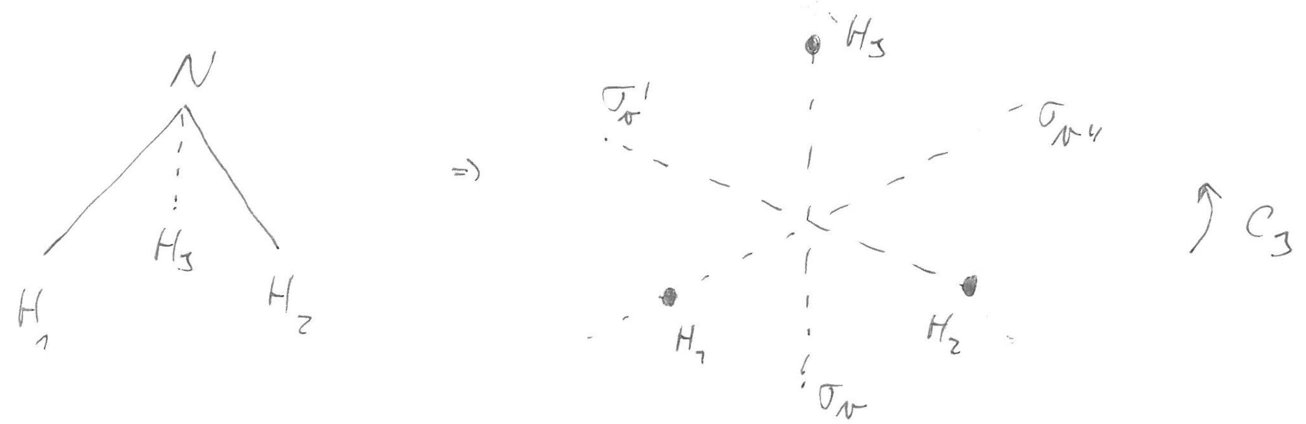
POINT GROUPS

- finite subgroups of $O(3)$ / $E(3)$
- transformations preserving distances and position of one fixed point (usually origin)

Example: C_{3v} - symmetry group of NH_3



- in each allowed transformation, equivalent atoms are permuted among themselves (i.e., we can't distinguish the orientation before & after

symmetry elements	$\Leftrightarrow$	sym. operations
3 mirror planes σ_v		reflections σ_v
1 proper rotation axis C_3 (rotation by $\frac{2\pi}{3}$)		rotations C_3, C_3^2
		identity $E = C_3^3 = \sigma_v^2$

$\left.\begin{matrix}\sigma_v \\ C_3, C_3^2 \\ E\end{matrix}\right\}$ elements of C_{3v}

C_{3v}:

E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v'	σ_v	C_3^2	C_3	E

$$C_3\sigma_v\begin{pmatrix} & 3 & \\ 1 & & 2\end{pmatrix} = C_3\begin{pmatrix} & 3 & \\ 2 & & 1\end{pmatrix} = \begin{pmatrix} & 1 & \\ 3 & & 2\end{pmatrix}$$

$$\sigma_v C_3\begin{pmatrix} & 3 & \\ 1 & & 2\end{pmatrix} = \sigma_v\begin{pmatrix} & 2 & \\ 3 & & 1\end{pmatrix} = \begin{pmatrix} & 2 & \\ 1 & & 3\end{pmatrix}$$

$\Rightarrow$ it's ~~on~~ our non-abelian 6-element group

- $C_{3v} \sim Sym(3)$:

$$E \leftrightarrow (1\,2\,3) \qquad \sigma_v \leftrightarrow (2\,1\,3)$$
$$C_3 \leftrightarrow (2\,3\,1) \qquad \sigma_v' \leftrightarrow (3\,2\,1)$$
$$C_3^2 \leftrightarrow (3\,1\,2) \qquad \sigma_v'' \leftrightarrow (1\,3\,2)$$

- subgroups of C_{3v}:
  - $C_s = \{E, \sigma_v\} \sim \{E, \sigma_v'\} \sim \{E, \sigma_v''\}$
  - $C_3 = \{E, C_3, C_3^2\}$

- left cosets with respect to C_3:

  $\sigma_v C_3 = \{\sigma_v, \sigma_v', \sigma_v''\}$ & C_3 itself

- left cosets with resp. to $\{E, \sigma_v\}$:

  $C_3 C_s = \{C_3, \sigma_v'\}$

  $C_3^2 C_s = \{C_3^2, \sigma_v''\}$

  C_s itself

- classes of C_{3v}: (exercise)

$$(E) = \{E\}$$
$$(C_3) = \{C_3, C_3^2\}$$
$$(\sigma_v) = \{\sigma_v, \sigma_v', \sigma_v''\}$$

  - classes are composed of symmetry operations associated with equivalent sym. elements – i.e., elements that can be transformed between themselves by same sym. operation from the group:

    → rotating σ_v plane by $\frac{2\pi}{3}$ ($\equiv C_3$) gives σ_v'' plane etc.

More on symmetry elements

- (proper) rotation axis C_n (rotation by $\varphi = \frac{2\pi}{n}$)

  $\Rightarrow$ operations $C_n, C_n^2, \ldots, C_n^{n-1}$ (might coincide with other operations, e.g., $C_4^2 = C_2$)

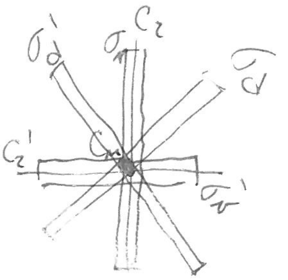
  - main axis – axis with the largest n (order of rot.)

- mirror planes $\sigma_v, \sigma_d, \sigma_h$

  σ_h ... perpendicular to main axis

  σ_v, σ_d ... // with C_n

  σ_d vs. σ_v: if $\exists\, n \times C_2 \perp C_n$, then

  1, σ_v is parallel to C_n and one of C_2

  2, σ_d (dihedral) is parallel to C_n an divides the angle between two C_2 in half

- improper rotation axis S_n (rotation by $\frac{2\pi}{n}$ plus reflection through the plane perpendicular to the axis)

  $\Rightarrow$ operations $S_n, S_n^3, \ldots, S_n^{2n-1}$ (even S_n^{2m} are C_n^{2m}) for odd n

- inversion center i $\Rightarrow$ operation $i \equiv (x_i \to -x_i)$ (only the origin)

note: • $\sigma = S_1$, $i = S_2$ $\Rightarrow$ the only operations are in fact proper & improper rotations

- existence of some symmetry elements can imply existence of others (C_n & $C_2 \perp C_n$ $\Rightarrow$ another $(n-1)$ C_2 axes, but there are also more complicated relationships)

Point groups classification:

1, only one rot. axis of order n $\Rightarrow$ group $\boxed{C_n}$

2, $C_n + n \times C_2 \perp C_n \Rightarrow \boxed{D_n}$ (dihedral)

3, $C_n + \sigma_h \Rightarrow \boxed{C_{nh}} + n \times C_2 \perp C_n \Rightarrow \boxed{D_{nh}}$

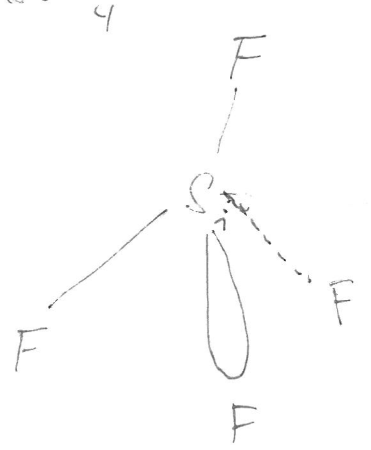
4, $C_n + \overset{n\times}{\vee}\sigma_v = \boxed{C_{nv}} + n \times C_2 \perp C_n \Rightarrow \boxed{D_{nv}}$

5, $C_n + S_{2n} \parallel C_n \Rightarrow \boxed{S_{2n}}$ (S_{2n} can't $\exists$ without C_n)

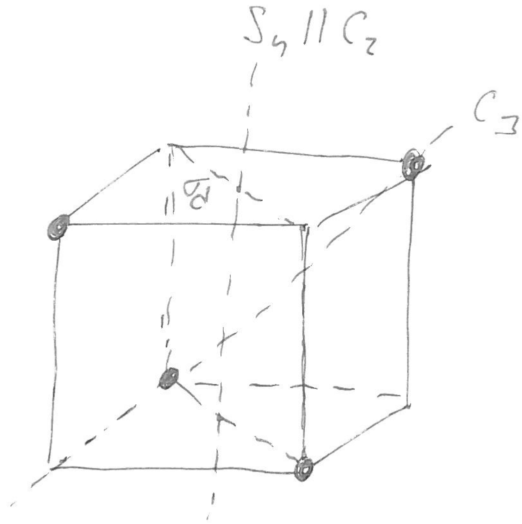
6, $C_n + i$: $\cdot\, n = 1 \Rightarrow C_i \sim C_s \sim S_2$

$\cdot\, n > 1 \Rightarrow$ something above

SiF_4 - silicon tetrafluoride



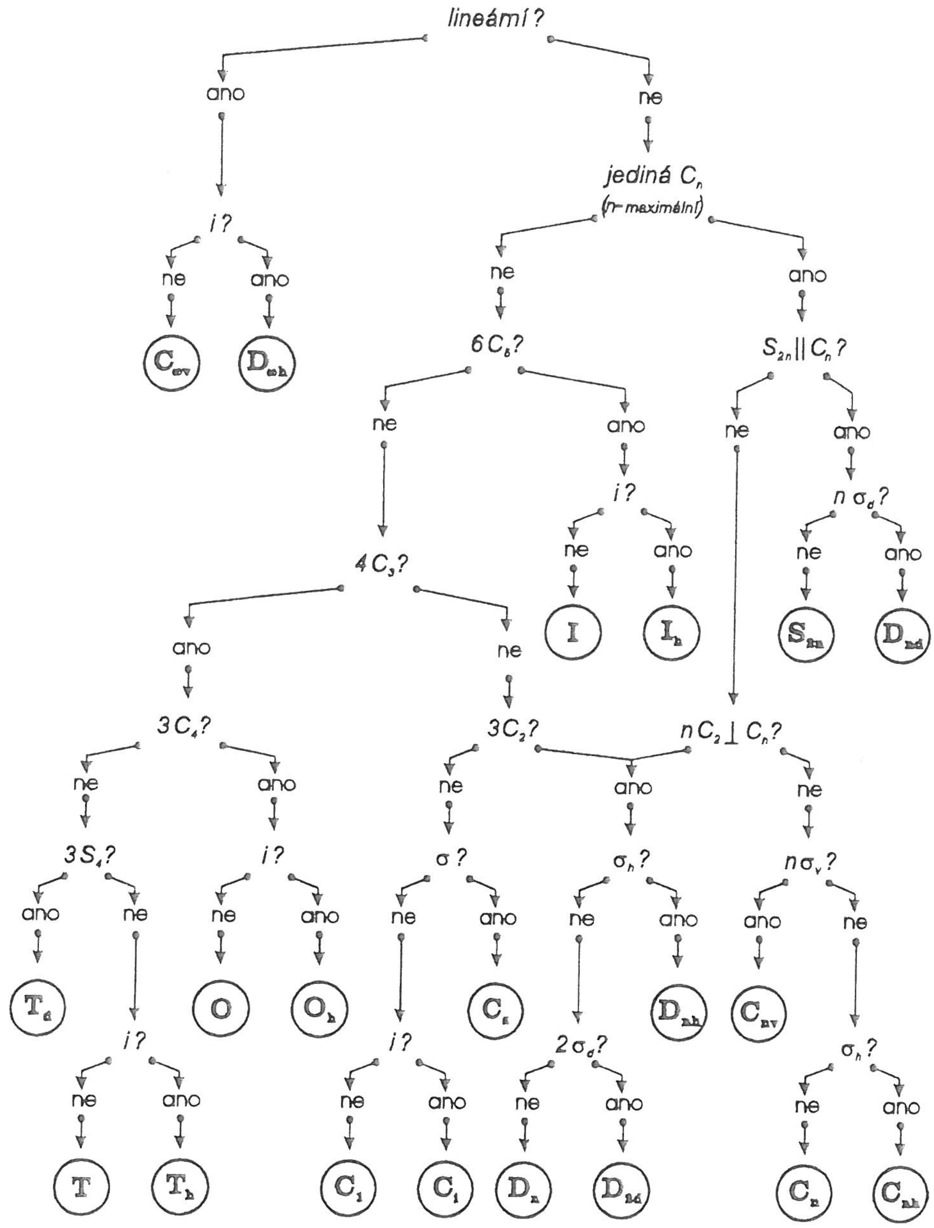
"put into a cube"

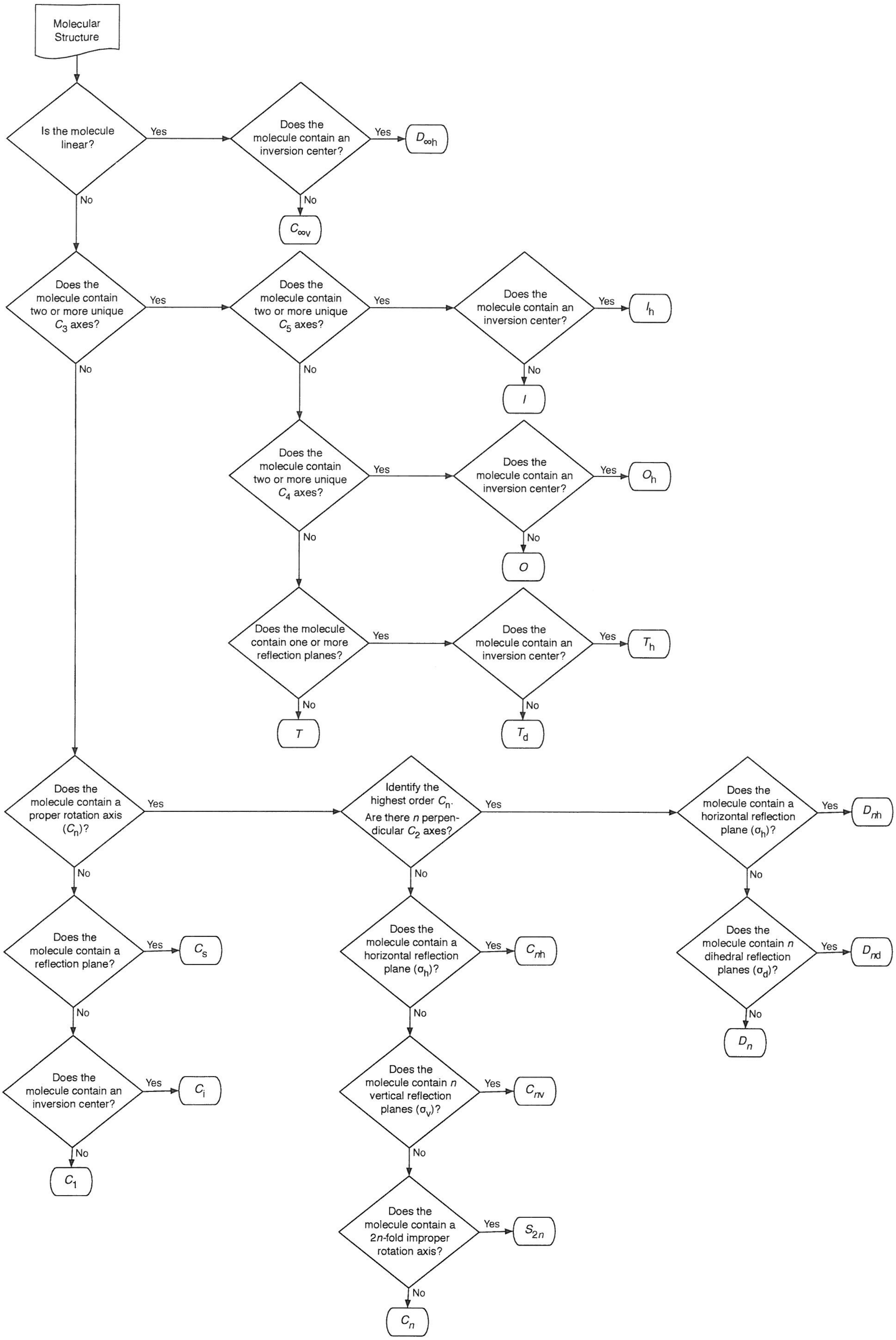


lin? no $\rightarrow$ two or more $C_{n>2}$? yes $4\times C_3$ $\rightarrow$ inversion? no

$$\Rightarrow T_d = \{E, 4\times C_3, 4\times C_3^2, 3\times C_2, 4\times S_4, 4\times S_4^3, 6\times\sigma_d\}$$

10.3. Schéma k určení bodové grupy symetrie





Molecular Structure
Is the molecule linear?
Yes
No
Does the molecule contain an inversion center?
Yes
No
$D_{\infty h}$
$C_{\infty v}$
Does the molecule contain two or more unique C_3 axes?
Does the molecule contain two or more unique C_5 axes?
Does the molecule contain an inversion center?
I_h
I
Does the molecule contain two or more unique C_4 axes?
Does the molecule contain an inversion center?
O_h
O
Does the molecule contain one or more reflection planes?
Does the molecule contain an inversion center?
T_h
T
T_d
Does the molecule contain a proper rotation axis (C_n)?
Identify the highest order C_n. Are there n perpendicular C_2 axes?
Does the molecule contain a horizontal reflection plane (σ_h)?
D_{nh}
Does the molecule contain n dihedral reflection planes (σ_d)?
D_{nd}
D_n
Does the molecule contain a reflection plane?
C_s
Does the molecule contain an inversion center?
C_i
C_1
Does the molecule contain a horizontal reflection plane (σ_h)?
C_{nh}
Does the molecule contain n vertical reflection planes (σ_v)?
C_{nv}
Does the molecule contain a $2n$-fold improper rotation axis?
S_{2n}
C_n