Notes of **Advanced Physical Chemistry II**

hebrewsnabla

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Contents

Introduction

TA: 刘琼 G403

12 Group Theory: the Exploitation of Symmetry

Matrices

$\det(\mathbf{A}) = 0 \;\Rightarrow\; \mathbf{A}$ is a singular matrix.

12.1 The Exploitation of the Symm of a Mol Can Be Used to Significantly Simplify Numerical Calculations

12.2 The Symm of Mols Can Be Described by a Set of Symm Elements

E	
C_n	Rotation by $360°/n$
σ	
i	
S_n	

Table 1: Symmetry elements and operators

Identity

Rotation

σ_h	horizontal
σ_v	vertical
σ_d	diagonal (vertical and bisects the angle between C_2 axis)

Table 2

Reflection

Inversion

Rotation Reflection

$$\hat{S}_n = \hat{\sigma}_h \times \hat{C}_n \tag{12.1}$$

12.2.1 Point Groups of Interest to Chemists

C_{nv}	
C_{nh}	Rotation by $360°/n$
D_{nh}	
D_{nv}	
D_{nd}	
T_d	

Table 3: Symmetry elements and operators

12.3 The Symm Operators of a Mol Form a Group

A set of operators form a group if they satisfy:

1. closed under multiplication 乘法封闭
2. associative multiplication 乘法结合律
3. only one identity operator 单位元
4. everyone has only one inverse 逆元

12.3.1 Point Group for Some Mols

No Symm Axis
C_1 – nothing
C_s – σ
C_i – i

C_n

S_n

C_{nv} – C_n and $n\sigma_v$

C_{nh} – C_n and σ_h

D_n – C_n and $nC_2 \perp C_n$
e.g. 一点点交错的 C_3H_6, C_2 在 3 个角平分线处

D_{nd} – C_n(also S_{2n}) and $nC_2 \perp C_n$ and $n\sigma_d$

D_{nh} – C_n and $nC_2 \perp C_n$ and σ_h

T_d 主轴是 S_4

O_h

I_h

12.4 Symm Operators Can Be Represented by Matrices

12.5 The C_{3v} Point Group Has a 2-D Irreducible Representation

12.6 The Most Important Summary of the Properties of a Point Group Is Its Character Table

$$\sum_R D_{il}^{(\nu)} D_{jm}^{*(\mu)} = \frac{g}{n_\nu} \delta_{\mu\nu} \delta_{ij} \delta_{lm} \tag{12.2}$$

$$\sum_R \chi^{(\nu)}(R) \chi^{*(\mu)}(R) = g \delta_{\mu\nu} \tag{12.3}$$