

Contents

Preface — V

List of Tables — XIII

List of Figures — XV

List of Notation — XVII

1 Introduction — 1

2 Some mathematical fundamentals — 6

2.1 Vector spaces — 6

2.1.1 The sum of subspaces — 7

2.1.2 The tensor product of two vector spaces — 9

2.2 Pre-Hilbert spaces — 10

2.3 Affine spaces — 12

2.4 Equivalence relations — 13

2.5 Linear functions — 14

2.5.1 Endomorphisms — 18

2.5.2 Isomorphisms and automorphisms — 23

2.6 Kronecker product of matrices — 24

Part I: Groups

3 Groups — 29

3.1 Groups — 29

3.2 Subgroups — 31

3.2.1 Conjugate subgroups — 31

3.2.2 The normalizer of a subgroup — 32

3.2.3 Subgroups generated by a set — 33

3.3 The direct product of groups — 34

3.4 Conjugacy classes — 35

3.5 Cosets and factor groups — 38

3.6 Group homomorphisms — 41

3.6.1 Group isomorphisms — 43

3.6.2 Homomorphism theorem — 45

3.7 The matrix groups $\mathbf{GL}(n, \mathbb{K})$ — 46

3.8	The automorphism groups $\mathbf{Aut}(\mathbb{V})$ —	47
3.9	Symmetrical groups $S_{\mathcal{X}}$ —	48
4	The action of a group —	52
5	The representation of a group —	55
5.1	Representations —	55
5.1.1	Linear representations —	55
5.1.2	Matrix representations —	56
5.1.3	The direct sum of linear representations —	57
5.2	Decomposition of representations —	59
5.3	Equivalent representations —	62
6	The character of a linear representation —	69
6.1	The character of a representation —	69
6.2	Class functions —	70
6.3	The character of a direct sum of linear representations —	74
7	The regular representation and consequences —	78
7.1	The dimension formula —	79
7.2	The number of the irreducible representations —	80

Part II: Isometry groups

8	The isometry group $\mathcal{I}(\mathbb{V}_n)$ —	85
8.1	The isometries on $\mathbb{V}_n$ —	85
8.2	The isometry group $\mathcal{I}(\mathbb{V}_n)$ —	89
9	The isometry group $\mathcal{I}_0(\mathbb{V}_2)$ —	91
9.1	The isometries on $\mathbb{V}_2$ —	91
9.2	The group $\mathcal{O}(2)$ —	93
10	The isometry group $\mathcal{I}_0(\mathbb{R}^3)$ —	101
10.1	The rotations on $\mathbb{R}^3$ —	101
10.1.1	Rotation matrices —	102
10.1.2	Properties of the rotation matrices —	106
10.2	The group $\mathcal{SO}(3)$ —	111
10.3	The improper rotations on $\mathbb{R}^3$ —	113
10.3.1	Improper rotation matrices —	115
10.3.2	Properties of the improper rotation matrices —	117
10.4	The group $\mathcal{O}(3)$ —	119

- 10.5 The isometry group $\mathcal{I}_0(\mathbb{R}^3)$ — 122
- 10.5.1 The product of two isometries — 126
- 10.5.2 Commuting isometries — 130
- 10.5.3 Conjugate isometries — 131

Part III: The symmetry of molecules

- 11 The symmetry of molecules — 137**
 - 11.1 The symmetry of a figure in $\mathbb{R}^n$ — 137
 - 11.2 The symmetry of a nuclear configuration — 141
 - 11.3 Similar nuclear configurations — 145
 - 11.4 The symmetry elements — 146
 - 11.5 Requirements — 148
- 12 Point groups of molecules — 149**
 - 12.1 The cyclic groups — 149
 - 12.1.1 The groups C_n — 149
 - 12.1.2 The group C_s — 150
 - 12.1.3 The groups S_n — 150
 - 12.2 The groups C_{nh} and C_{nv} — 151
 - 12.2.1 The groups C_{nh} — 151
 - 12.2.2 The groups C_{nv} — 152
 - 12.3 The dihedral groups — 157
 - 12.3.1 The groups D_n — 157
 - 12.3.2 The groups D_{nh} — 160
 - 12.3.3 The groups D_{nd} — 165

Part IV: Symmetry in molecular systems

- 13 The configuration space of a molecular system — 175**
 - 13.1 The configuration space $\mathbb{P}_n$ — 176
 - 13.2 The space $\mathbb{T}$ of overall translations — 179
 - 13.3 The configuration subspace $\mathbb{P}_0$ — 180
 - 13.4 The configuration subspace $\mathbb{L}_0(d)$ — 181
 - 13.5 The space of infinitesimal rotations — 182
- 14 Symmetry in a configuration space — 188**
 - 14.1 The linear representation $\hat{\Gamma}_n$ — 189
 - 14.1.1 The matrix representation Γ_n — 189
 - 14.1.2 The linear representation $\hat{\Gamma}_n$ — 193

- 14.1.3 Properties of the linear representation $\hat{\Gamma}_n$ — **196**
- 14.2 The symmetry of a point — **197**
- 14.3 Fixed-point subspaces — **199**
- 14.4 The dimension of a fixed-point subspace — **209**

- 15 The energy function of a molecular system — 214**
- 15.1 Gradient and Hessian matrix of an energy function — **215**
- 15.2 Gradient and Hessian matrix at G-symmetric points — **220**
- 15.3 Stationary points of an energy function — **223**
- 15.4 Reduced energy functions on fixed-point subspaces — **225**

Part V: Symmetry breaking in molecular systems

- 16 Symmetry breaking in a molecular system — 231**
- 16.1 Bifurcation subgroups — **231**
- 16.2 Bifurcation subgroups and characters — **245**
- 16.2.1 Normal bifurcation subgroups — **245**
- 16.2.2 Nonnormal bifurcation subgroups — **247**

- 17 The bifurcation subgroups of some Abelian point groups — 255**
- 17.1 The bifurcation subgroups of the groups C_n , C_s and S_{2n} — **255**
- 17.2 The bifurcation subgroups of the groups C_{nh} — **258**

- 18 The bifurcation subgroups of the groups C_{nv} — 261**
- 18.1 Some nonnormal subgroups of the groups C_{nv} — **261**
- 18.1.1 The subgroups C_v and C'_v — **261**
- 18.1.2 The subgroups C_{2v} and C'_{2v} — **264**
- 18.2 The normal bifurcation subgroups of the groups C_{nv} — **267**
- 18.3 The nonnormal bifurcation subgroups of the groups C_{nv} , $n = 3, \dots, 6$ — **270**
- 18.3.1 Group C_{3v} — **271**
- 18.3.2 Group C_{4v} — **272**
- 18.3.3 Group C_{5v} — **273**
- 18.3.4 Group C_{6v} — **274**

- 19 The bifurcation subgroups of the groups D_n — 277**
- 19.1 The normal bifurcation subgroups of the groups D_n — **277**
- 19.2 The nonnormal bifurcation subgroups of the groups D_n , $n = 3, \dots, 6$ — **280**
- 19.2.1 Group D_3 — **282**
- 19.2.2 Group D_4 — **282**
- 19.2.3 Group D_5 — **283**
- 19.2.4 Group D_6 — **285**

20	The bifurcation subgroups of the groups D_{nh} — 289
20.1	Two group automorphisms — 289
20.1.1	Group automorphism Φ_1 — 289
20.1.2	Group automorphism Φ_2 — 290
20.2	Some nonnormal subgroups of the groups D_{nh} — 290
20.2.1	Groups C_v and C'_2 — 292
20.2.2	Groups C_{2v} and D_2 — 293
20.2.3	Groups C'_{2v} and C''_{2v} — 295
20.2.4	Groups C'_{2h} and C''_{2h} — 297
20.2.5	Groups D_{2h} and $D^{(1)}_{2h}$ — 299
20.3	The irreducible representations of the groups D_{nh} — 301
20.4	The normal bifurcation subgroups of the groups D_{nh} — 307
20.5	The nonnormal bifurcation subgroups of the groups D_{nh} , $n = 3, \dots, 6$ — 309
20.5.1	Group D_{3h} — 311
20.5.2	Group D_{4h} — 312
20.5.3	Group D_{5h} — 314
20.5.4	Group D_{6h} — 316
21	The bifurcation subgroups of the groups D_{nd} — 320
21.1	A group automorphism — 320
21.2	Some nonnormal subgroups of the groups D_{nd} — 321
21.2.1	Groups C'_2 and $C^{(n)}_d$ — 322
21.2.2	Groups D_2 and $\hat{C}^{(n)}_{2v}$ — 323
21.2.3	Groups D_3 and $\hat{C}^{(6)}_{3v}$ — 325
21.2.4	Groups $\hat{C}^{(n)}_{2h}$ — 328
21.2.5	Groups $D^{(n)}_{2d}$ — 329
21.3	The normal bifurcation subgroups of the groups D_{nd} — 335
21.4	The nonnormal bifurcation subgroups of the groups D_{nd} , $n = 2, \dots, 6$ — 338
21.4.1	Group D_{2d} — 339
21.4.2	Group D_{3d} — 341
21.4.3	Group D_{4d} — 342
21.4.4	Group D_{5d} — 345
21.4.5	Group D_{6d} — 347

Part VI: Equilibrial paths and symmetry breaking

22	Equilibrial reaction paths — 357
22.1	Equilibrial paths — 358
22.1.1	The function h_0 — 359
22.1.2	The zero set of the function h_0 — 362

22.2	Symmetric regular paths —	369
22.2.1	Equivariant functions —	369
22.2.2	Symmetry conservation —	371
22.2.3	Reduced functions —	374
23	Symmetry breaking at an equilibrial path —	380
23.1	Simple bifurcation points —	380
23.2	Symmetry breaking bifurcation points —	381

Part VII: Chemical reactions

24	A mathematical model of chemically reacting systems —	391
24.1	Preliminaries —	391
24.2	Transition configurations —	393
24.2.1	Definition of transition configurations —	393
24.2.2	Saddle points —	397
24.2.3	Valley-ridge-inflection points —	398
24.3	A classification of chemical reactions —	400
24.3.1	Chemical reactions of Type I —	402
24.3.2	Chemical reactions of Type II —	402
24.3.3	Chemical reactions of Type III —	410
25	Examples —	411
25.1	Ammonia —	412
25.2	Xenon tetrafluoride —	425
25.3	Ozone —	441
25.4	Formaldehyde —	448

A The symmetry types — 459

Bibliography — 461

Index — 463