Contents

Preface *page* xi

1 Introduction 1
- 1.1 Calculation of potential energy surfaces 5
- 1.2 Clusters 8
- 1.3 Proteins 30
- 1.4 Glasses and supercooled liquids 66

References 104

2 The Born–Oppenheimer approximation and normal modes 119
- 2.1 Independent degrees of freedom 119
- 2.2 The Born–Oppenheimer approximation 121
- 2.3 The simplest PES: a diatomic molecule 123
- 2.4 Breakdown of the Born–Oppenheimer approximation 126
- 2.5 Nuclear dynamics 135

References 157

3 Symmetry considerations 161
- 3.1 Essential results from group theory 161
- 3.2 The molecular symmetry group 163
- 3.3 The molecular symmetry group of a rigid molecule 165
- 3.4 Molecular symmetry groups for nonrigid molecules 170
- 3.5 Continuous symmetry measures 172
- 3.6 Polytetrahedral packing and bulk systems 178
- 3.7 Localised and delocalised states 186

References 189

4 Features of the landscape 192
- 4.1 Classification of stationary points 192
- 4.2 Properties of steepest-descent pathways 196
- 4.3 Classification of rearrangements 209
- 4.4 Branch points 211

4.5 Tunnelling 219
4.6 Pathways and coordinate transformations 229
4.7 Zero Hessian eigenvalues 233
References 237
5 Describing the landscape 241
5.1 How many stationary points are there? 242
5.2 Monotonic sequences 246
5.3 Disconnectivity graphs 250
5.4 Small worlds 276
References 280
6 Exploring the landscape 283
6.1 Finding local minima 283
6.2 Finding transition states 284
6.3 Finding higher index saddles 298
6.4 Coordinate systems and constraints 300
6.5 Sampling thermodynamic properties 304
6.6 Sampling dynamical properties 316
6.7 Global optimisation 330
References 352
7 Properties of the landscape 364
7.1 The superposition approximation 365
7.2 Transition states and dynamics 384
7.3 Sampling stationary points 394
7.4 Kinetic Monte Carlo and related schemes 395
7.5 Discrete path sampling 397
7.6 Catastrophe theory 410
7.7 Chaotic dynamics and the potential energy surface 424
References 428
8 Clusters 434
8.1 Finite size phase transitions 434
8.2 Thermodynamics and cluster simulation 452
8.3 Lennard-Jones clusters 455
8.4 Morse clusters 480
8.5 Alkali halide clusters 492
8.6 Annealing of buckminsterfullerene 501
8.7 Water clusters 511
References 523
9 Biomolecules 530
9.1 Computer simulations 531
9.2 Protein structure prediction 535

9.3 Models of protein folding 540
9.4 Random energy models and frustration 546
9.5 Calculated free energy surfaces 551
9.6 An off-lattice bead model 557
9.7 The IAN tetrapeptide 565
9.8 The NATA and NATMA dipeptides 571
9.9 Polyalanine peptides 573
References 584
10 Glasses and supercooled liquids 592
10.1 Theories of the glass transition 592
10.2 Simulations of structural glasses 615
10.3 Superposition methods for glasses 624
10.4 Transition states and pathways 633
10.5 Analysis of model potential energy landscapes 645
10.6 Peculiarities of large systems 653
References 654
Appendix A Sylvester's law of inertia 663
Appendix B Derivation of $\Omega(E, \mathbf{P}, \mathbf{L})$ 665
Index 671