CONTENTS

Preface xi

1 What Is Density Functional Theory? 1

1.1 How to Approach This Book, 1

1.2 Examples of DFT in Action, 2

1.2.1 Ammonia Synthesis by Heterogeneous Catalysis, 2

1.2.2 Embrittlement of Metals by Trace Impurities, 4

1.2.3 Materials Properties for Modeling Planetary Formation, 6

1.3 The Schrödinger Equation, 7

1.4 Density Functional Theory—From Wave Functions to Electron Density, 10

1.5 Exchange–Correlation Functional, 14

1.6 The Quantum Chemistry Tourist, 16

1.6.1 Localized and Spatially Extended Functions, 16

1.6.2 Wave-Function-Based Methods, 18

1.6.3 Hartree–Fock Method, 19

1.6.4 Beyond Hartree–Fock, 23

1.7 What Can DFT Not Do?, 28

1.8 Density Functional Theory in Other Fields, 30

1.9 How to Approach This Book (Revisited), 30

References, 31

Further Reading, 32
2 DFT Calculations for Simple Solids
2.1 Periodic Structures, Supercells, and Lattice Parameters, 35
2.2 Face-Centered Cubic Materials, 39
2.3 Hexagonal Close-Packed Materials, 41
2.4 Crystal Structure Prediction, 43
2.5 Phase Transformations, 44
Exercises, 46
Further Reading, 47
Appendix Calculation Details, 47

3 Nuts and Bolts of DFT Calculations
3.1 Reciprocal Space and $k$ Points, 50
  3.1.1 Plane Waves and the Brillouin Zone, 50
  3.1.2 Integrals in $k$ Space, 53
  3.1.3 Choosing $k$ Points in the Brillouin Zone, 55
  3.1.4 Metals—Special Cases in $k$ Space, 59
  3.1.5 Summary of $k$ Space, 60
3.2 Energy Cutoffs, 61
  3.2.1 Pseudopotentials, 63
3.3 Numerical Optimization, 65
  3.3.1 Optimization in One Dimension, 65
  3.3.2 Optimization in More than One Dimension, 69
  3.3.3 What Do I Really Need to Know about Optimization?, 73
3.4 DFT Total Energies—An Iterative Optimization Problem, 73
3.5 Geometry Optimization, 75
  3.5.1 Internal Degrees of Freedom, 75
  3.5.2 Geometry Optimization with Constrained Atoms, 78
  3.5.3 Optimizing Supercell Volume and Shape, 78
Exercises, 79
References, 80
Further Reading, 80
Appendix Calculation Details, 81

4 DFT Calculations for Surfaces of Solids
4.1 Importance of Surfaces, 83
4.2 Periodic Boundary Conditions and Slab Models, 84
4.3 Choosing $k$ Points for Surface Calculations, 87
4.4 Classification of Surfaces by Miller Indices, 88
4.5 Surface Relaxation, 94
4.6 Calculation of Surface Energies, 96
CONTENTS

7 Equilibrium Phase Diagrams from Ab Initio Thermodynamics 163

7.1 Stability of Bulk Metal Oxides, 164
   7.1.1 Examples Including Disorder—Configurational Entropy, 169
7.2 Stability of Metal and Metal Oxide Surfaces, 172
7.3 Multiple Chemical Potentials and Coupled Chemical Reactions, 174
Exercises, 175
References, 176
Further Reading, 176
Appendix Calculation Details, 177

8 Electronic Structure and Magnetic Properties 179

8.1 Electronic Density of States, 179
8.2 Local Density of States and Atomic Charges, 186
8.3 Magnetism, 188
Exercises, 190
Further Reading, 191
Appendix Calculation Details, 192

9 Ab Initio Molecular Dynamics 193

9.1 Classical Molecular Dynamics, 193
   9.1.1 Molecular Dynamics with Constant Energy, 193
   9.1.2 Molecular Dynamics in the Canonical Ensemble, 196
   9.1.3 Practical Aspects of Classical Molecular Dynamics, 197
9.2 Ab Initio Molecular Dynamics, 198
9.3 Applications of Ab Initio Molecular Dynamics, 201
   9.3.1 Exploring Structurally Complex Materials: Liquids and Amorphous Phases, 201
   9.3.2 Exploring Complex Energy Surfaces, 204
Exercises, 207
Reference, 207
Further Reading, 207
Appendix Calculation Details, 208
10 Accuracy and Methods beyond “Standard” Calculations

10.1 How Accurate Are DFT Calculations?, 209
10.2 Choosing a Functional, 215
10.3 Examples of Physical Accuracy, 220
   10.3.1 Benchmark Calculations for Molecular Systems—Energy and Geometry, 220
   10.3.2 Benchmark Calculations for Molecular Systems—Vibrational Frequencies, 221
   10.3.3 Crystal Structures and Cohesive Energies, 222
   10.3.4 Adsorption Energies and Bond Strengths, 223
10.4 DFT+X Methods for Improved Treatment of Electron Correlation, 224
   10.4.1 Dispersion Interactions and DFT-D, 225
   10.4.2 Self-Interaction Error, Strongly Correlated Electron Systems, and DFT+U, 227
10.5 Larger System Sizes with Linear Scaling Methods and Classical Force Fields, 229
10.6 Conclusion, 230
References, 231
Further Reading, 232

Index