

Contents

Notation	xv
1 Computational materials modelling from first principles	1
1.1 Density functional theory	2
1.2 Examples of materials modelling from first principles	3
1.3 Timeline of DFT calculations in materials modelling	13
1.4 Reasons behind the popularity of density functional theory	16
1.5 Atomistic materials modelling and emergent properties	17
2 Many-body Schrödinger equation	19
2.1 The Coulomb interaction	19
2.2 Many-body Schrödinger equation	20
2.3 Atomic units	23
2.4 Clamped nuclei approximation	25
2.5 Independent electrons approximation	27
2.6 Exclusion principle	29
2.7 Mean-field approximation	30
2.8 Hartree–Fock equations	32
2.9 Kohn–Sham equations	35
3 Density functional theory	36
3.1 Total energy of the electronic ground state	36
3.2 Kohn–Sham equations	39
3.3 The local density approximation	40
3.4 Self-consistent calculations	46
3.5 Remit of density functional theory and limitations	49
4 Equilibrium structures of materials: fundamentals	51
4.1 The adiabatic approximation	51
4.2 Atomic forces	54
4.3 Calculating atomic forces using classical electrostatics	59
4.4 How to find the equilibrium configuration using calculated forces	62
5 Equilibrium structures of materials: calculations vs. experiment	66
5.1 Structure of molecules	66
5.2 Structure of crystals	69
5.3 Comparison of DFT structures with X-ray crystallography	72
5.4 Structure of surfaces	76
5.5 Comparison of DFT surface reconstructions with STM	80
6 Elastic properties of materials	87
6.1 Elastic deformations	87
6.2 Intuitive notions of stress and strain using computer experiments	88
6.3 General formalism for the elastic properties of solids	91
6.4 Calculating elastic constants using the DFT total energy	94

6.5	Examples of calculations of elastic constants	96
6.6	The stress theorem	98
6.7	DFT predictions for materials under extreme conditions	99
7	Vibrations of molecules and solids	102
7.1	Heuristic notion of atomic vibrations	102
7.2	Formal theory of vibrations for classical nuclei	106
7.3	Calculations of vibrational eigenmodes and eigenfrequencies	111
7.4	Vibrations of crystalline solids	115
8	Phonons, vibrational spectroscopy and thermodynamics	123
8.1	Basics of Raman and neutron scattering spectroscopy	123
8.2	Going beyond the classical approximation for nuclei	131
8.3	Vibrons and phonons	137
8.4	Phonon density of states	140
8.5	Phonon DOS and pressure-temperature phase diagrams	142
9	Band structures and photoelectron spectroscopy	152
9.1	Kohn-Sham energies and wavefunctions	152
9.2	Calculation of band structures using DFT	155
9.3	Basics of angle-resolved photoelectron spectroscopy	162
9.4	Metals, insulators and semiconductors	168
9.5	The band gap problem	173
10	Dielectric function and optical spectra	177
10.1	The dielectric function of a model solid	177
10.2	General properties of the dielectric function	189
10.3	Using DFT to calculate dielectric functions	193
10.4	Advanced concepts in the theory of the dielectric function	204
11	Density functional theory and magnetic materials	207
11.1	The Dirac equation and the concept of spin	207
11.2	Charge density and spin density	214
11.3	Spin in a system with many electrons	220
11.4	Spin and exchange energy	222
11.5	Spin in density functional theory	227
11.6	Examples of spin-DFT calculations	230
Appendix A	Derivation of the Hartree-Fock equations	239
Appendix B	Derivation of the Kohn-Sham equations	243
Appendix C	Numerical solution of the Kohn-Sham equations	246
Appendix D	Reciprocal lattice and Brillouin zone	254
Appendix E	Pseudopotentials	258
References		264
Index		284