

Contents

<i>Preface</i>	<i>page</i> viii
1 Setting the stage: why <i>ab initio</i> molecular dynamics?	1
Part I Basic techniques	9
2 Getting started: unifying MD and electronic structure	11
2.1 Deriving classical molecular dynamics	11
2.2 Ehrenfest molecular dynamics	22
2.3 Born–Oppenheimer molecular dynamics	24
2.4 Car–Parrinello molecular dynamics	27
2.5 What about Hellmann–Feynman forces?	51
2.6 Which method to choose?	56
2.7 Electronic structure methods	67
2.8 Basis sets	75
3 Implementation: using the plane wave basis set	85
3.1 Introduction and basic definitions	85
3.2 Electrostatic energy	93
3.3 Exchange and correlation energy	99
3.4 Total energy, gradients, and stress tensor	104
3.5 Energy and force calculations in practice	109
3.6 Optimizing the Kohn–Sham orbitals	111
3.7 Molecular dynamics	119
3.8 Program organization and layout	128
4 Atoms with plane waves: accurate pseudopotentials	136
4.1 Why pseudopotentials?	137
4.2 Norm-conserving pseudopotentials	138
4.3 Pseudopotentials in the plane wave basis	152
4.4 Dual-space Gaussian pseudopotentials	157

4.5	Nonlinear core correction	160
4.6	Pseudopotential transferability	162
4.7	Example: pseudopotentials for carbon	167
Part II Advanced techniques		175
5	Beyond standard <i>ab initio</i> molecular dynamics	177
5.1	Introduction	177
5.2	Beyond microcanonics: thermostats, barostats, meta-dynamics	178
5.3	Beyond ground states: ROKS, surface hopping, FEMD, TDDFT	194
5.4	Beyond classical nuclei: path integrals and quantum corrections	233
5.5	Hybrid QM/MM molecular dynamics	267
6	Beyond norm-conserving pseudopotentials	286
6.1	Introduction	286
6.2	The PAW transformation	287
6.3	Expectation values	290
6.4	Ultrasoft pseudopotentials	292
6.5	PAW energy expression	296
6.6	Integrating the Car–Parrinello equations	297
7	Computing properties	309
7.1	Perturbation theory: Hessian, polarizability, NMR	309
7.2	Wannier functions: dipole moments, IR spectra, atomic charges	327
8	Parallel computing	350
8.1	Introduction	350
8.2	Data structures	352
8.3	Computational kernels	354
8.4	Massively parallel processing	359
Part III Applications		369
9	From materials to biomolecules	371
9.1	Introduction	371
9.2	Solids, minerals, materials, and polymers	372
9.3	Interfaces	376
9.4	Mechanochemistry and molecular electronics	380
9.5	Water and aqueous solutions	382

9.6	Non-aqueous liquids and solutions	385
9.7	Glasses and amorphous systems	389
9.8	Matter at extreme conditions	390
9.9	Clusters, fullerenes, and nanotubes	392
9.10	Complex and fluxional molecules	394
9.11	Chemical reactions and transformations	396
9.12	Homogeneous catalysis and zeolites	399
9.13	Photophysics and photochemistry	400
9.14	Biophysics and biochemistry	403
10	Properties from <i>ab initio</i> simulations	407
10.1	Introduction	407
10.2	Electronic structure analyses	407
10.3	Infrared spectroscopy	410
10.4	Magnetism, NMR and EPR spectroscopy	411
10.5	Electronic spectroscopy and redox properties	412
10.6	X-ray diffraction and Compton scattering	413
10.7	External electric fields	414
11	Outlook	416
	<i>Bibliography</i>	419
	<i>Index</i>	550