Contents

List of abbreviations		xiii
1	Introduction1.1 A survey of time-dependent phenomena1.2 Preview of and guide to this book	1 1 7
2	Review of ground-state density-functional theory 2.1 The formal framework of DFT 2.2 Exact properties 2.3 Approximate functionals PART I THE BASIC FORMALISM OF TDDFT	10 11 21 30
3	Fundamental existence theorems 3.1 Time-dependent many-body systems 3.2 The Runge–Gross theorem 3.3 The van Leeuwen theorem	45 45 50 54
4	The time-dependent Kohn-Sham scheme 4.1 The time-dependent Kohn-Sham equation 4.2 Spin-dependent systems 4.3 The adiabatic approximation 4.4 The meaning of self-consistency in DFT and TDDFT 4.5 Numerical time propagation	59 59 61 62 65
5	Time-dependent observables 5.1 Explicit density functionals 5.2 Implicit density functionals 5.3 The time-dependent energy	73 73 81 88
6	Properties of the time-dependent xc potential 6.1 What is the universal xc functional? 6.2 Some exact conditions 6.3 Galilean invariance and the harmonic potential theorem 6.4 Memory and causality 6.5 Initial-state dependence 6.6 Time-dependent variational principles 6.7 Discontinuity upon change of particle number	91 91 93 98 103 107 111

x Contents

PART II LINEAR RESPONSE AND EXCITATION ENERGIES

7	The formal framework of linear-response TDDFT	123
	7.1 General linear-response theory	124
	7.2 Spectroscopic observables	132
	7.3 Linear density response in TDDFT	137
	7.4 Warm-up exercise: TDDFT for two-level systems	143
	7.5 Calculation of excitation energies: the Casida equation	145
	7.6 The Tamm–Dancoff approximation and other simplifications	151
	7.7 Excitation energies with time-dependent Hartree–Fock theory	153
8	The frequency-dependent xc kernel	157
	8.1 Exact properties	157
	8.2 Approximations	163
	8.3 The xc kernels of the homogeneous electron liquid	164
9	Applications to atomic and molecular systems	176
	9.1 Excitation energies of small systems: basic trends and features	177
	9.2 Molecular excited-state properties with TDDFT: an overview	182
	9.3 Double excitations	189
	9.4 Charge-transfer excitations	195
	9.5 The Sternheimer equation	202
	9.6 Optical spectra via time propagation schemes	204
	PART III FURTHER DEVELOPMENTS	
10	Time-dependent current-DFT	213
	10.1 The adiabatic approximation and beyond	213
	10.2 The failure of nonadiabatic local approximations in TDDFT	215
	10.3 The formal framework of TDCDFT	218
	10.4 The VK functional	225
	10.5 Applications of TDCDFT in the linear-response regime	231
	10.6 Memory effects: elasticity and dissipation	241
11	The time-dependent optimized effective potential	252
	11.1 The static OEP approach for orbital functionals	253
	11.2 The TDOEP scheme	263
	11.3 TDOEP in the linear regime	276
12	Extended systems	279
	12.1 Electronic structure and excitations of periodic solids	279
	12.2 Spectroscopy of density fluctuations: plasmons	285
	12.3 Optical absorption and excitons	289
	12.4 TDCDFT in periodic systems	299
13	v v	304
	13.1 Perturbation theory along the adiabatic connection	304
	13.2 Nonequilibrium Green's functions and the Keldysh action	308
	13.3 xc kernels from many-body theory	318

	PART IV SPECIAL TOPICS	
14	Long-range correlations and dispersion interactions	333
	14.1 The adiabatic-connection fluctuation—dissipation approach	333
	14.2 Van der Waals interactions	340
15	Nanoscale transport and molecular junctions	351
	15.1 Basic concepts	352
	15.2 Transport in the linear-response limit	355
	15.3 Finite-bias and non-steady-state transport	360
16	Strong-field phenomena and optimal control	374
	16.1 Multiphoton ionization	376
	16.2 High-order harmonic generation	386
	16.3 Optimal control	388
17	Nuclear motion	394
	17.1 Potential-energy surfaces	394
	17.2 Ab initio molecular dynamics	401
	17.3 Multicomponent TDDFT	413
$\mathbf{A}\mathbf{p}$	pendix A Atomic units	416
	A.1 Atomic units in vacuum	416
	A.2 Atomic units in the effective-mass approximation	417
Ap	pendix B Functionals and functional derivatives	419
Ap	pendix C Densities and density matrices	422
Ap	pendix D Hartree–Fock and other wave-function approaches	425
$\mathbf{A}\mathbf{p}$	pendix E Constructing the xc potential from a given density	429
	E.1 Ground-state densities	429
	E.2 Time-dependent densities	431
$\mathbf{A}\mathbf{p}$	pendix F DFT for excited states	434
	F.1 Generalized Kohn–Sham schemes for excited states	434
	F.2 Ensemble formalism	436
$\mathbf{A}\mathbf{p}$	pendix G Systems with noncollinear spins	439
	G.1 DFT for noncollinear spins	439
	G.2 Linear response and excitation energies	440
Ap	pendix H The dipole approximation	445
	H.1 Interaction with electromagnetic waves	445
	H.2 Dipole matrix elements and dipole moments	447
Ap	pendix I A brief review of classical fluid dynamics	450
	I.1 Basics and ideal fluids	450
	I.2 Viscous fluids and dissipation	452

xii Contents

Appendix J Constructing the scalar xc kernel from the tensor	
xc kernel	455
Appendix K Semiconductor quantum wells	458
K.1 Effective-mass approximation and subband levels	459
K.2 Intersubband dynamics	462
Appendix L TDDFT in a Lagrangian frame	465
L.1 Fluid motion in the Lagrangian and laboratory frames	466
L.2 TDDFT in the Lagrangian frame	469
L.3 The small-deformation approximation	471
L.4 The nonlinear elastic approximation	473
L.5 Validity of the VK potential and breakdown of the adiabatic	
approximation	474
Appendix M Inversion of the dielectric matrix	477
Appendix N Review literature on DFT and many-body theory	479
Appendix O TDDFT computer codes	482
References	484
Index	