Contents

1. Introduction 1

2. Basic Formalism for Stationary Non-Relativistic Systems 4
2.1 The Hohenberg-Kohn Theorem 4
2.2 Degenerate Groundstates 7
2.3 v-Representability and Related Questions 10
2.4 Fractional Particle Number, Chemical Potential, and Derivative Discontinuities 19

3. Extensions 25
3.1 Spin-Polarised Systems 25
3.2 Finite Temperature Ensembles 28
3.3 Multicomponent Systems 30
3.4 Hartree-Fock Limit 31
3.5 Excited States 32
3.6 Density Matrix Functionals 36
3.7 Momentum Space 37
3.8 Bose Systems 39
3.9 Superconducting Systems 39

4. The Kohn-Sham Scheme 43
4.1 The Basic Kohn-Sham Equations 44
4.2 Degenerate Kohn-Sham Groundstates and the Question of v-Representability 48
4.3 Spin-Polarised Systems 52
4.4 Fractional Occupation, Janak's Theorem, and the Slater Transition State 54
4.5 Excited States: The Kohn-Sham Scheme for Ensembles 58
4.6 Schrödinger Equation for the Square Root of the Groundstate Density 62
4.7 Hellmann-Feynman, Virial, and Scaling Properties of Density Functionals 64
4.8 Single-Particle Equations for Superconductors: A Generalized Bogoliubov-deGennes Scheme 70

5. Explicit Functionals I: Kinetic and Exchange Energy Functionals Derived from the One-Particle Density Matrix 75
5.1 Density-Gradient Expansions from Semiclassical Expansions: A Survey 75
5.2 The Kirzhnits Method 79
5.2.1 Semiclassical Expansion 79
5.2.2 Density-Gradient Expansion 83
5.3 The Wigner-Kirkwood Approach and Partial Resummation of the Gradient Expansion 90
5.4 Empirical Convergence Studies of the Gradient Expansion ... 95
5.5 Original von Weizsäcker Functional Versus Gradient Expansion 105
5.6 Padé Approximants and Other Parametrisations 113
5.7 Phase-Space Approach Based on Local Thermodynamics 120
5.8 The Classical Density Functional Models of Thomas, Fermi, Dirac, and von Weizsäcker 124
5.8.1 Definition of the Models 124
5.8.2 The Thomas-Fermi Variational Equation 126
5.8.3 Numerical Comparison and Some Applications 131

6. Many-Body Perturbation Theory 138
6.1 Diagrammatic Approach to the Inhomogeneous Electron Gas 139
6.2 The Exchange-Correlation Functional Expressed in Terms of the Irreducible Self-Energy 142
6.3 The Band Gap in Insulators and Semiconductors 145
6.4 The Fermi Surface in Metals 148
6.5 The Homogeneous Electron Gas 149
6.5.1 Basic Relations 149
6.5.2 The Groundstate Energy 162

7. Explicit Functionals II: The Local Density Approximation and Beyond 173
7.1 The Local Density Approximation 176
7.2 Discussion of the Local Density Approximation 183
7.3 Nonlocal Density Schemes 188
7.4 Self-Interaction Corrections 192
7.5 Wave Vector Analysis 196
7.6 Gradient Corrections 199
7.6.1 General Considerations 199
7.6.2 Low-Order Perturbative Results 204
7.6.3 Hartree-Fock Results 207
7.6.4 Results Based on Random Phase and Related Approximations 214
7.6.5 Results Derived from the Local Field Correction 220
7.6.6 Results Based on Wave Vector Analysis 222
7.7 Kohn-Sham Results for Atoms and Molecules 229

7.7.1 Atomic Systems 230
7.7.2 Molecular Systems 238

8. Density Functional Theory of Relativistic Systems 245
8.1 Introduction 245
8.2 Existence Theorems 246
8.3 Explicit Functionals I: The Relativistic Kirzhnits Expansion .. 251
8.3.1 The Dirac Orbital Picture 252
8.3.2 The Quantum Electrodynamical Picture 257
8.4 The Homogeneous Relativistic Electron Gas 261
8.5 Explicit Functionals II: The Local Density Approximation ... 264
8.5.1 Unpolarised Systems 264
8.5.2 Polarised Systems 266
8.6 Remarks and Applications 269

Appendix 273
A. Definition of Density Matrices, Green's Functions, and Correlation Functions 273
B. Compilation of Literature on Atomic and Molecular Kohn-Sham Results 277

References 281

Subject Index 297