Contents

1. Introduction 1

2. Overview 7
2.1 k–Mass 10
2.2 Electrons in Metals 12
2.2.1 Jellium Model 13
2.3 Electron Fluctuations (Plasmons) 16
2.4 Electron–Plasmon Coupling 16
2.5 ω–Mass 20
2.6 Total Effective Mass 21
2.7 Induced Interaction 21
2.8 Examples 23
2.9 Minimal Mean Field Theory 23
2.9.1 Non-locality in Space of the Exchange Contribution . . . 24
2.9.2 Non-locality in Time of the Correlation Contribution . 26
2.10 Phonons 26
2.11 Appendix 28
2.11.1 Second Quantization 28
2.11.2 Single-Particle Self-Energy 32

3. Electronic Structure 35
3.1 Born–Oppenheimer Approximation 35
3.2 Density Functional Theory: Generalities 38
3.3 The Local Density Approximation 41
3.3.1 Discussion of Kohn–Sham Method 43
3.3.2 Pseudopotentials 44
3.4 Kohn–Sham Equations in a Spherical Basis 45
3.4.1 The Expansion of V_{ext} in Spherical Harmonics 47
3.4.2 The Expansion of $\varrho(\boldsymbol{r})$, v_{H} and v_{xc} 50
3.5 Kohn–Sham Equations in a Cylindrical Basis 51
3.6 Appendices 54
3.6.1 Basics on Pseudopotentials 54
3.6.2 Matrix Elements in a Spherical Basis 57

4. Electronic Response to Time-Dependent Perturbations ... 61
4.1 Linear Response: RPA and TDLDA ... 61
4.2 Strength Function and Sum Rules ... 65
4.3 Transition Density and Plasmons ... 68
4.4 Appendices ... 70
4.4.1 Linear Response ... 70
4.4.2 TDLDA or RPA in the Configuration Space ... 72
4.4.3 Plasmon Wavefunction Components for a Separable Interaction ... 73
4.4.4 Spherical TDLDA ... 74
4.4.5 Cylindrical TDLDA ... 76

5. Applications to Carbon Structures and Metal Clusters ... 79
5.1 C_{60} Fullerene ... 79
5.1.1 Kohn–Sham States for C_{60} ... 79
5.1.2 The Optical Absorption of C_{60} ... 81
5.2 Carbon Nanotubes ... 85
5.2.1 Electronic Structure ... 86
5.2.2 Electromagnetic Response and Static Polarizabilities ... 87
5.3 Linear Carbon Chains ... 89
5.3.1 Electronic Structure ... 89
5.3.2 Optical Response and Plasmon Resonances ... 93
5.4 Metal Clusters: the Case of Na_8 ... 98
5.5 Appendices ... 100
5.5.1 Role of Symmetries ... 100

6. Phonons: Harmonic Approximation ... 105
6.1 Harmonic Approximation ... 106
6.1.1 A Practical Example: a Linear Triatomic Molecule ... 111
6.2 Phonon Calculations ... 112
6.2.1 Introduction ... 112
6.2.2 Bond Charge Models ... 114
6.2.3 Phonons from ab initio Calculations ... 128

7. The Car–Parrinello Method ... 131
7.1 An Efficient Tool for Solving the Electronic Problem ... 131
7.2 Car–Parrinello Molecular Dynamics ... 133
7.3 Ionic Motion: Parameter-Free Molecular Dynamics Simulation 136
7.3.1 Frozen-Phonon Calculations ... 141

8. Coupling of Electrons to Phonons and to Plasmons ... 145
8.1 Definition of the Electron–Phonon Interaction ... 146
8.2 Diagonal Matrix Elements ... 148
8.3 Electron–Phonon Coupling in C_{60}^- ... 149

8.4 Signatures of the Electron–Phonon Interaction: Photoemission in C_{60}^{-} 154
8.4.1 Electron–Phonon Coupling in Other Fullerenes 160
8.4.2 Electron–Phonon Coupling in Sodium Clusters 163
8.5 The Effective Electron–Electron Interaction 165
8.6 Coupling of Electrons to Plasmons 166
8.7 TDLDA with Electron–Plasmon and Electron–Phonon Couplings 169
8.8 An Example: Electron–Phonon and Electron–Plasmon Couplings in Na_9^{+} 171
8.9 Appendices 173
8.9.1 Terms Neglected in the Born–Oppenheimer Approximation 173
8.9.2 The Electron–Phonon Coupling Constant λ 175
8.9.3 Outline of the Derivation of (8.50) 177
8.9.4 Equation (8.50) Using Second-Order Perturbation Theory 178

9. Pairing in Atomic Aggregates 183
9.1 The BCS Solution 184
9.2 Superconductivity in Metals 190
9.2.1 Finite Temperature 190
9.3 Superconductivity in Fullerides 194
9.3.1 C_{60} Fullerene Based Superconductors 195
9.3.2 Nanometer Superconductors Based on Small Fullerenes 197
9.3.3 Thin Carbon Nanotubes 200
9.4 Selected Open Questions 201
9.4.1 Hole Doped Fullerites 202
9.4.2 Screening Effects 204
9.5 Appendices 204
9.5.1 Simple Estimate of μ 204
9.5.2 Solution of the Pairing Hamiltonian 206
9.5.3 Temperature Dependent BCS Solution 213

10. Discussion 221

References 224

Index 233