C. Fiolhais F. Nogueira M. Marques (Eds.)

A Primer in Density Functional Theory

Springer

Table of Contents

1 Density Functionals for Non-relativistic Coulomb Systems in the New Century	
John P. Perdew, Stefan Kurth	1
1.1 Introduction	1
1.1.1 Quantum Mechanical Many-Electron Problem	1
1.1.2 Summary of Kohn–Sham Spin-Density Functional Theory...	2
1.2 Wavefunction Theory	5
1.2.1 Wavefunctions and Their Interpretation	5
1.2.2 Wavefunctions for Non-interacting Electrons	7
1.2.3 Wavefunction Variational Principle	8
1.2.4 Hellmann–Feynman Theorem	9
1.2.5 Virial Theorem	10
1.3 Definitions of Density Functionals	11
1.3.1 Introduction to Density Functionals	11
1.3.2 Density Variational Principle	12
1.3.3 Kohn–Sham Non-interacting System	13
1.3.4 Exchange Energy and Correlation Energy	14
1.3.5 Coupling-Constant Integration	16
1.4 Formal Properties of Functionals	20
1.4.1 Uniform Coordinate Scaling	20
1.4.2 Local Lower Bounds	22
1.4.3 Spin Scaling Relations	23
1.4.4 Size Consistency	23
1.4.5 Derivative Discontinuity	24
1.5 Uniform Electron Gas	25
1.5.1 Kinetic Energy	25
1.5.2 Exchange Energy	26
1.5.3 Correlation Energy	27
1.5.4 Linear Response	29
1.5.5 Clumping and Adiabatic Connection	32
1.6 Local, Semi-local and Non-local Approximations	32

1.6.1	Local Spin Density Approximation	32
1.6.2	Gradient Expansion	36
1.6.3	History of Several Generalized Gradient Approximations	40
1.6.4	Construction of a “GGA Made Simple”	42
1.6.5	GGA Nonlocality: Its Character, Origins, and Effects	44
1.6.6	Hybrid Functionals	49
1.6.7	Meta-generalized Gradient Approximations	50
1.6.8	Jacob’s Ladder of Density Functional Approximations	51
2	Orbital-Dependent Functionals for the Exchange-Correlation Energy: A Third Generation of Density Functionals	
	Eberhard Engel	56
2.1	Introduction	56
2.1.1	Preliminaries and Notation	57
2.1.2	Motivation for Orbital-Dependent Functionals	59
2.1.3	Basic Concept of Orbital-Dependent Functionals	63
2.2	Optimized Potential Method (OPM)	64
2.2.1	Direct Functional Derivative	65
2.2.2	Total Energy Minimization	66
2.2.3	Invariance of the Density	67
2.2.4	Exact Relations Related to OPM	70
2.2.5	Krieger–Li–Iafrate Approximation	71
2.3	Exchange-Only Results	73
2.3.1	Accuracy of the KLI Approximation	73
2.3.2	Properties of the Exact Exchange: Comparison with Explicit Density Functionals	31
2.4	First-Principles Implicit Correlation Functionals	90
2.4.1	Many-Body Theory on the Basis of the Kohn–Sham System: Exact Expression for E_{xc}	90
2.4.2	Perturbative Approach to the Sham–Schlüter Equation: Second Order Correlation Functional	94
2.4.3	Extensions of the Second Order Functional	97
2.5	Semi-empirical Orbital-Dependent Exchange-Correlation Functionals	99
2.5.1	Self-interaction Corrected LDA	99
2.5.2	Colle–Salvetti Functional	100
2.6	Analysis of the Orbital-Dependent Correlation	101
2.6.1	Description of Dispersion Forces by Second Order Correlation Functional	101
2.6.2	Comparison of Available Orbital-Dependent Approximations for E_c	106
2.6.3	Analysis of the Second Order Correlation Potential	111
2.7	Final Remarks	117

3 Relativistic Density Functional Theory

Reiner Dreizler	123
3.1 Summary	123
3.2 Foundations	126
3.3 Functionals	129
3.4 Results	136
3.5 Further Results	140

4 Time-Dependent Density Functional Theory

Miguel A.L. Marques, Eberhard K.U. Gross	144
4.1 Introduction	144
4.2 Time-Dependent DFT	145
4.2.1 Preliminaries	145
4.2.2 The Runge–Gross Theorem	148
4.2.3 Time-Dependent Kohn–Sham Equations	151
4.2.4 XC Functionals	153
4.2.5 Numerical Considerations	156
4.3 Linear Response Theory	158
4.3.1 Basic Theory	158
4.3.2 The XC Kernel	161
4.4 Excitation Energies	164
4.4.1 DFT Techniques to Calculate Excitations	164
4.4.2 Full Solution of the Kohn–Sham Equations	166
4.4.3 Excitations from Linear-Response Theory	168
4.4.4 When Does It Not Work?	173
4.5 Atoms and Molecules in Strong Laser Fields	174
4.5.1 What Is a “Strong” Laser?	174
4.5.2 High-Harmonic Generation	176
4.5.3 Multi-photon Ionization	177
4.5.4 Ionization Yields from TDDFT	179
4.6 Conclusion	181

5 Density Functional Theories and Self-energy Approaches

Rex W. Godby, Pablo García-González	185
5.1 Introduction	185
5.2 Many-Body Perturbation Theory	186
5.2.1 Green’s Function and Self-energy Operator	186
5.2.2 Many-Body Perturbation Theory and the <i>GW</i> Approximation	189
5.3 Pathologies of the Kohn–Sham xc Functional	194
5.3.1 The Band Gap Problem	196
5.3.2 Widely Separated Open Shell Atoms	199
5.3.3 The Exchange–Correlation Electric Field	200
5.4 Total Energies from Many-Body Theory	203

5.4.1	Theoretical Background	203
5.4.2	Applications	207
5.4.3	Generalised KS Schemes and Self-energy Models	212
5.5	Concluding Remarks	214
6	A Tutorial on Density Functional Theory	
	Fernando Nogueira, Alberto Castro, Miguel A.L. Marques	218
6.1	Introduction	218
6.2	Solving the Kohn-Sham Equations	219
6.2.1	Generalities	219
6.2.2	Atoms	224
6.2.3	Plane-Waves	225
6.2.4	Real-Space	229
6.3	Pseudo-potentials	230
6.3.1	The Pseudo-potential Concept	230
6.3.2	Empirical Pseudo-potentials	232
6.3.3	<i>Ab-initio</i> Pseudo-potentials	233
6.3.4	Hamann Potential	234
6.3.5	Troullier-Martins Potential	235
6.3.6	Non-local Core Corrections	236
6.3.7	Pseudo-potential Transferability	237
6.3.8	Kleinman and Bylander Form of the Pseudo-potential	238
6.4	Atomic Calculations	239
6.5	Plane-Wave Calculations	244
6.6	Real-Space Calculations	251