

Eberhard Engel
Reiner M. Dreizler

Theoretical and Mathematical Physics

Density Functional Theory

An Advanced Course

 Springer

Density Functional Theory

Theoretical and Mathematical Physics

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Density Functional Theory

An Advanced Course

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Preface

This book emerged from a course on density functional theory (DFT), first given at the University of Munich more than a decade ago. The course was based on the classic texts by Dreizler and Gross (Springer, 1990) and by Parr and Yang (Oxford University Press, 1989). More recent topics of that time, such as time-dependent DFT or orbital-dependent functionals, were added to the material covered by the two books. However, already at that time restriction to the most relevant and/or most illustrative statements on a particular aspect of DFT was necessary, in order to keep the length of the course under control. When the course was later given again at the University of Frankfurt it soon turned out to be impossible to integrate the exploding number of new results, concerning both the formalism as well as important applications, into the course: So, even a selection of the branches of DFT covered in the course was unavoidable.

The present text reflects this, admittedly subjective, choice of topics: it concentrates on the basics of the most widely used variants of DFT. This implies a thorough discussion of the corresponding existence theorems and effective single-particle equations as well as of the key approximations utilized in implementations. Ground state DFT (on the nonrelativistic level) is addressed in Chaps. 2–6. Chapter 2 introduces the fundamental Hohenberg-Kohn theorem and its extensions to spin-, current- and current-spin-density functional theory, together with some basic notions such as v -representability. The resulting Kohn-Sham equations are collected in Chap. 3. This chapter also includes a discussion of the relation between the Kohn-Sham wavefunctions and eigenvalues and the true many-body wavefunctions and energies. Chapter 4 is devoted to a detailed exposition of the currently available approximations for the exchange-correlation functional, based on two exact representations of this quantity. The most important virial relations valid for density functionals are summarized in Chap. 5. The discussion of the exchange-correlation functional is then resumed in Chap. 6, in which the concept of orbital-dependent functionals is introduced. This chapter also serves as a demonstration of the first-principles character of DFT, in that it shows that the true exchange-correlation energies and potentials can be systematically approached by use of orbital-dependent functionals. On the other hand, the discussion of the existence theorem, of the basic

formalism and of standard approximations is concentrated in a single chapter in the case of time-dependent DFT (Chap. 7). The same statement applies to relativistic DFT which is presented in Chap. 8. An extended review of the problem of renormalization (in the Appendices F–I) serves as background information for relativistic DFT.

Throughout the text formal statements are complemented by selected quantitative results, which primarily aim at an illustration of the strengths and weaknesses of a particular approach or functional. However, no attempt is made to review the full range of present-day DFT applications, not even their boundaries will be marked out. In order to stay within reasonable bounds, the discussion also omits a few topics which have recently attracted much interest, such as DFT for superconducting or hadronic systems. An overview of the topics not covered explicitly in this book is provided by Chap. 9 (*Further Reading*) which offers a substantial collection of pertinent papers together with some comments.

The students in the courses indicated above had quite diverse backgrounds, ranging from mineralogy to biochemistry. So, the courses had to be rather self-contained, requiring neither the audience's familiarity with standard many-body theory nor extensive experience with the quantum theory of solids. Again, the book reflects this fact: the reader will find that all concepts of many-body theory which are indispensable for the discussion of DFT, such as the single-particle Green's function or response functions, are introduced step by step, rather than just used. The same applies to some basic notions of solid state theory, as, for instance, the Fermi surface. In fact, even the language of second quantization is introduced systematically in an Appendix. When starting with this Appendix, reading this book should require little more than a strong background in elementary quantum mechanics (at least, if one accepts some of the more advanced relations of Chap. 4 without going through their derivations¹).

As is clear from these remarks, this book does not target only one particular scientific community. On the other hand, the material is easily restricted to the needs of a more specialized course. Many of the advanced chapters require little more than knowledge of the most elementary parts of the introductory chapters. Several redundancies help to support this modular structure. It should therefore be possible to find one's own way through the material. Although detailed recommendations have obvious problems, some suggestions for selected reading are made in the following table:

¹ An alternative, low level entry point to the discussion of the exchange-correlation energy functional is provided by Appendix D, in which the local density approximation for the exchange functional is derived explicitly without using concepts from many-body theory. With the background of this appendix it should be possible to continue with the more advanced results and explicit functionals of Chap. 4.

Section	Bias solid state physics		Bias chemistry, atomic physics	
	Basic	Advanced	Basic	Advanced
1	Complete		Complete	
2.1	Complete	Complete	Complete	Complete
2.2	Optional	Complete	Optional	Complete
2.3	1.+2. paragraph	Complete	1.+2. paragraph	Complete
2.4		Complete		Complete
2.5	Complete	Complete	Complete	Complete
2.6		Optional		Optional
2.7	Complete	Complete	Complete	Complete
3.1	Complete	Complete	Complete	Complete
3.2,3.3		Complete		Complete
3.4		Optional		Optional
3.5	Complete	Complete	Complete	Complete
3.6	Complete	Complete	1st paragraph	3.6.1
3.7		Optional		Optional
4.1	Complete	Complete	Complete	Complete
4.2	Only results	Complete		Only results
4.3	Complete	Complete	App.D+4.3.2–6	Complete
4.4	Only results	Complete		Only results
4.5	4.5.4+4.5.5	Complete	4.5.4+4.5.5	Complete
4.6				
4.7		Optional		Optional
4.8	Optional	Complete		Only results
4.9	Complete	Complete		
5.1–5.4	Complete	Complete	Complete	Complete
6.1	Complete	Complete	Complete	Complete
6.2	6.2.1/2/5/6	6.2.1–6		6.2.1/2/5/6
6.3	Complete	Complete		Complete
6.4		6.4.1+6.4.2		6.4.1
6.5		6.5.4	6.5.4	6.5.4
6.6		Complete		Complete
6.7				
7.1–7.6	Complete	Complete	Complete	Complete
8.1		Complete		Complete
8.2–8.5		Optional		
8.6		Complete		Complete
8.7		Complete		Optional
8.8		Optional		Optional

Depending on the background of the reader, Appendix B (on second quantization) might have to be included between Chaps. 1 and 2.

At various points explicit derivations of important results are given, rather than just summaries of the results. These derivations might not be suitable for presenta-

tion in a course, depending on its scope and audience. However, there is always an option to skip the details and restrict oneself to the essentials. Sometimes, such details are distinguished from the main text by use of a smaller font, in other cases the details have been relegated to Appendices. At some points the reader will find suggestions which portion of the text may be skipped, if one wants to focus on results only.

It is a pleasure for us to acknowledge the help and support that we received when writing this book. This book has benefited enormously from extensive discussions with Dr. D. Ködderitzsch. His comments and suggestions helped in particular to improve the readability of this text for less experienced readers. Many thanks go to the two referees of our manuscript (unknown to us). Their reports encouraged us to include a number of additional topics in the text (some suggested by the referees, others which we felt appropriate), although this led to an increase of its length, way beyond initial plans. Equally important, however, was the additional time which the referees comments have given us: this allowed us to straighten out some paragraphs in the initial manuscript. We would also like to thank Dr. S. Varga and H. Engel for their careful proof-reading and many suggestions for improvements. We are grateful to M. Hellgren and U. von Barth for making their atomic RPA potentials available to us. Last, but not least, our thanks go to Dr. Ch. Caron from Springer Verlag, who supervised the production of this book. His support, flexibility and patience were instrumental in making this book what it is.

Frankfurt am Main,
March 2010

Eberhard Engel
Reiner M. Dreizler

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Acronyms

ALDA	adiabatic local density approximation
AF	antiferromagnetic
ASA	atomic sphere approximation
B86	Becke 86 GGA for exchange energy
B88	Becke 88 GGA for exchange energy
B3LYP	hybrid constructed on basis of Becke-Lee-Yang-Parr GGA
BLYP	Becke-Lee-Yang-Parr GGA
bcc	body-centered cubic
BO	Born-Oppenheimer
C	Coulomb
CDFT	current density functional theory
CS	Colle-Salvetti
CSDFT	current spin density functional theory
DC	Dirac-Coulomb
DCB	Dirac-Coulomb-Breit
DFT	density functional theory
DIR	direct (matrix element)
EA	electron affinity
ext	external
EXX	exact exchange
fcc	face-centered cubic
FP	full potential
GE	gradient expansion
GGA	generalized gradient approximation
GKS	generalized Kohn-Sham
GK	Gross-Kohn (kernel of TDDFT)
H	Hartree
HDL	high-density limit
HEG	homogeneous (or uniform) electron gas
HF	Hartree-Fock
HK	Hohenberg-Kohn

hom	homogeneous
HOMO	highest occupied molecular orbital
IP	ionization potential
int	interaction
ISI	interaction strength interpolation
KS	Kohn-Sham
KLI	Krieger-Li-Iafrate (approximation)
LAPW	linearized-augmented-plane-wave
LDA	local density approximation
LDA+ U	combination of LDA and Hubbard U approach
LH	local hybrid
LHF	localized Hartree-Fock
LM	Langreth-Mehl GGA for correlation energy
LR	linear response
LSDA	local spin-density approximation
LUMO	lowest unoccupied molecular orbital
LYP	Lee-Yang-Parr GGA
MGGA	meta generalized gradient approximation
MP	Møller-Plesset
np	no-pair
NR	nonrelativistic
OPM	optimized (effective) potential method
PP	pseudopotential
P86	Perdew 86 GGA for correlation energy
PBE	Perdew-Burke-Ernzerhof GGA
PBE0	hybrid constructed on basis of Perdew-Burke-Ernzerhof GGA
PKZB	Perdew-Kurth-Zupan-Blaha MGGA
PW86	Perdew-Wang 86 GGA for exchange energy
PW91	Perdew-Wang 91 GGA
PZ	Perdew-Zunger self-interaction correction
QED	quantum electrodynamics
R	retarded
RDFT	relativistic density functional theory
REXX	relativistic exact exchange
RHEG	relativistic homogeneous (or uniform) electron gas
RG	Runge-Gross (theorem)
RGGA	relativistic generalized gradient approximation
RHF	relativistic Hartree-Fock
RLDA	relativistic local density approximation
RLSDA	relativistic local spin density approximation
ROPM	relativistic optimized (effective) potential method
RPA	random phase approximation
RSDFT	relativistic spin density functional theory
SDFT	spin-density functional theory
s	single-particle, noninteracting, Kohn-Sham

SI	self-interaction
SIC	self-interaction correction
SOX	second order exchange
SPP	Stoll-Pavlidou-Preuss self-interaction correction
T	transverse
TDDFT	time-dependent density functional theory
TDKS	time-dependent Kohn-Sham
TDLDA	time-dependent local density approximation
TF	Thomas-Fermi
TPSS	Tao-Perdew-Staroverov-Scuseria MGGA
UV	ultraviolet
vBH	von Barth-Hedin LDA for correlation energy
VWN	Vosko-Wilk-Nusair LDA for correlation energy
WDA	weighted density approximation
xc	exchange-correlation

Chapter 1

Introduction

One of the basic problems in theoretical physics and chemistry is the description of the structure and dynamics of many-electron systems. These systems comprise single atoms, the most elementary building blocks of ordinary matter, all kinds of molecules, ranging from dimers to proteins, as well as mesoscopic systems, for example clusters or quantum dots, and solids, including layered structures, surfaces and quasi-crystals. The following two paragraphs list the properties of such systems which are generally of interest, without, however, aiming at completeness. These properties can roughly be classified as either structural or dynamical.

An important structural property is the electronic shell structure (or band structure in the case of crystals). The shell structure directly determines the stability of a system, but also shows up in a number of other properties—it is, for instance, a key factor in transport properties like the electrical conductivity. Stability manifests itself in various binding energies. These are either of electronic nature, such as the ionization potential and the work function, or they characterize the bonds between atoms, such as the atomization energy of molecules and the cohesive energy of solids. Other structural properties, which are related to shell structure, are electric or magnetic moments. The geometry of poly-atomic systems, that is bond lengths and bond angles as well as the symmetry of the atomic arrangement, constitutes yet another important structural property. Often several geometrical configurations which are almost degenerate (at least compared to typical thermal energies) are observed for such systems. In this case the relative stability of the various configurations is of obvious interest. All these properties have in common that they can be calculated if the relevant electronic ground states are known. Even if more than one ground state is involved, as in the comparison of energies of systems with different electron numbers or with different atomic configurations, there is no need to determine excited electronic states.

The electronic excitation spectrum is the most notable dynamical property. Excitation energies are not only the quantities necessary for an understanding of optical properties, they also feature in all kinds of scattering processes. In addition to the excitation spectrum, a complete description of excitation or ionization requires the evaluation of the associated transition probabilities. In a poly-atomic system the

excitation of nuclear motion is also possible, the rotational-vibrational motion in molecules or lattice vibrations (phonons) in solids being the simplest examples. The discussion of these dynamical properties obviously requires knowledge of either excited stationary states of the system, or even of time-dependent states.

For the study of these properties one can distinguish between two basic approaches:

1. The first approach is based on the true, fundamental Hamiltonian of the system. It is therefore called the *ab-initio* or *first principles* approach. As the solution of the resulting many-body Schrödinger equation is an extremely demanding task, some approximations are unavoidable. However, all approximations utilized in this context are of a technical nature, as for instance the determinantal form of the many-body wavefunction in the Hartree-Fock approximation or the representation of its single-particle ingredients in terms of a finite basis set. These technical simplifications can curtail the results of an *ab-initio* calculation: depending on the system and property under investigation, important features can be missed (e.g. a single-determinant wavefunction can not reproduce the fully correlated motion of the electrons). The *ab-initio* approach is thus not characterized by the absence of any approximations, but rather by the fact that the approximations do not introduce adjustable physical(!) parameters. Clearly, a more efficient technical approximation will lead to a computational task that can be handled more easily.
2. In the second approach a suitable *model* Hamiltonian is utilized from the very outset. Relying on available information (often experimental) on the system, the relevant aspects can be isolated and used to construct the model Hamiltonian. For instance, if one is interested in the magnetic ordering of a mono-atomic crystalline solid, one might rely on the *Heisenberg Hamiltonian*. In this model each atomic site α of the crystal is represented by a spin operator \mathbf{s}_α with possible eigenvalues corresponding to the available spin per site. The interaction between the spins of two sites α and β is represented by $-J\mathbf{s}_\alpha \cdot \mathbf{s}_\beta$, so that for positive J energy is gained by the alignment of the two spins. Clearly, the Heisenberg Spin Hamiltonian can not make any statement about the lattice constant of the solid, as it only deals with one particular property, its magnetism. The only remnant of the underlying electronic structure is the size of the coupling constant J . This physical parameter can, however, not be determined within the model, but has to be adjusted to experiment or some prior *ab-initio* results. The advantage of the use of model Hamiltonians is obvious: the resulting many-body problem is much simpler than the corresponding *ab-initio* problem. On the other hand, it is often an art to extract the essential aspects of a system in a way which neither ignores important features nor leads to an overwhelmingly complicated Hamiltonian.

The present text introduces a variant of the first approach, which is at the same time efficient, widely applicable and reasonably accurate.

The starting point of the discussion is the *ab-initio* Hamiltonian of the coupled electron-nucleus system,

$$\hat{H} = \hat{T}_n + \hat{V}_{n-n} + \hat{H}_e (+\hat{V}_{n\text{-field}}) \quad (1.1)$$

$$\hat{H}_e = \hat{T}_e + \hat{V}_{n-e} + \hat{V}_{e-e} (+\hat{V}_{e\text{-field}}). \quad (1.2)$$

In (1.1) \hat{T}_n represents the kinetic energy of the K nuclei of the system,

$$\hat{T}_n = \sum_{\alpha=1}^K \frac{(-i\hbar\nabla_{\mathbf{R}_\alpha})^2}{2M_\alpha}, \quad (1.3)$$

where \mathbf{R}_α denotes the Cartesian coordinates of nucleus α with mass M_α and $\nabla_{\mathbf{R}_\alpha} = \partial/\partial\mathbf{R}_\alpha$. The potential \hat{V}_{n-n} represents the repulsion among the nuclei,¹

$$\hat{V}_{n-n} = \sum_{\alpha,\beta=1;\alpha<\beta}^K \frac{Z_\alpha Z_\beta e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}. \quad (1.4)$$

For the electronic problem \hat{V}_{n-n} just amounts to an additive constant. The third component of \hat{H} is the electronic Hamiltonian \hat{H}_e , which is decomposed into the kinetic energy of the N electrons,

$$\hat{T}_e = \sum_{i=1}^N \frac{(-i\hbar\nabla_i)^2}{2m} \quad (1.5)$$

($\nabla_i \equiv \nabla_{\mathbf{r}_i}$, with \mathbf{r}_i denoting the position of electron i), the interaction between electrons and nuclei (with charges $Z_\alpha e$, $e = |e|$),

$$\hat{V}_{n-e} = - \sum_{\alpha=1}^K \sum_{i=1}^N \frac{Z_\alpha e^2}{|\mathbf{R}_\alpha - \mathbf{r}_i|}, \quad (1.6)$$

and the interaction among the electrons,

$$\hat{V}_{e-e} = \sum_{i,j=1;i<j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1.7)$$

Finally, depending on the system under consideration, the two types of particles can couple to an external electromagnetic field,

$$\hat{V}_{n\text{-field}} = \sum_{\alpha=1}^K \left[Z_\alpha e \Phi_{\text{ext}}(\mathbf{R}_\alpha t) + i \frac{Z_\alpha e \hbar}{M_\alpha c} \mathbf{A}_{\text{ext}}(\mathbf{R}_\alpha t) \cdot \nabla_{\mathbf{R}_\alpha} - \mathbf{I}_\alpha \cdot \mathbf{B}_{\text{ext}}(\mathbf{R}_\alpha t) \right] \quad (1.8)$$

$$\hat{V}_{e\text{-field}} = \sum_{i=1}^N \left[-e \Phi_{\text{ext}}(\mathbf{r}_i t) - 2i \mu_B \mathbf{A}_{\text{ext}}(\mathbf{r}_i t) \cdot \nabla_i + \mu_B \boldsymbol{\sigma}_i \cdot \mathbf{B}_{\text{ext}}(\mathbf{r}_i t) \right]. \quad (1.9)$$

Here $\Phi_{\text{ext}}(\mathbf{r}t)$ and $\mathbf{A}_{\text{ext}}(\mathbf{r}t)$ are the potentials corresponding to the electromagnetic field,

¹ Throughout this text we use Gaussian units for the electric charge.

$$\mathbf{E}_{\text{ext}}(\mathbf{r}t) = -\nabla\Phi_{\text{ext}}(\mathbf{r}t) - \frac{1}{c} \frac{\partial \mathbf{A}_{\text{ext}}(\mathbf{r}t)}{\partial t} \quad (1.10)$$

$$\mathbf{B}_{\text{ext}}(\mathbf{r}t) = \nabla \times \mathbf{A}_{\text{ext}}(\mathbf{r}t) . \quad (1.11)$$

I_α characterizes the magnetic moment of nucleus α , μ_B is the Bohr magneton, $\mu_B = e\hbar/(2mc)$, and $\boldsymbol{\sigma}_i$ the spin operator corresponding to electron i , (the vector $\boldsymbol{\sigma}$ denotes the three 2×2 Pauli matrices—for their explicit forms see Eqs. (2.122)–(2.124)).

A number of comments are appropriate:

- As expressed by (1.3) and (1.5), the motion of both the electrons and the nuclei is treated strictly nonrelativistically. Equations (1.3)–(1.9) also imply that the nuclei are point particles, characterized only by mass, charge and magnetic moment. Of course, the nonrelativistic and elementary treatment of the nuclei is completely legitimate for the range of questions addressed here. On the other hand, the neglect of all relativistic corrections to the kinetic energy of the electrons, most notably of the spin–orbit interaction, is not always legitimate: for heavy atoms relativistic effects modify the structure of the electronic Hamiltonian to an extent which is even noticeable in molecular bonds, so that use of a relativistic \hat{T}_e is required. The issue of relativity will be addressed in Chap. 8. For the time being the interest will, however, be restricted to the nonrelativistic limit.
- Similarly, the interaction between the charged particles in the Hamiltonians (1.4), (1.6) and (1.7) is given by the instantaneous and spin-independent Coulomb interaction, which ignores the transverse nature of light (photons) and its finite speed, manifest e.g. in the Breit interaction. The discussion of relativistic corrections to the Coulomb interaction is also postponed to Chap. 8. However, it seems worthwhile to emphasize already at this point that the neglect of the Breit corrections is in general much less critical than the neglect of the spin–orbit interaction.
- In Eqs. (1.1) and (1.2) the possible presence of an external electromagnetic field is indicated. This field can be either static or time-dependent, as for instance a laser pulse. Again the coupling of the field to the quantized particles is specified on the simplest level available, assuming Coulomb gauge,

$$\nabla \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}t) = 0 . \quad (1.12)$$

Most of the discussion will, however, be devoted to the field-free situation $\Phi_{\text{ext}} = \mathbf{A}_{\text{ext}} = 0$ or to static fields. The Hamiltonian of the coupled system is then stationary. Nevertheless, even in this case a time-dependence can be introduced into the electron problem as soon as the motion of the nuclei is treated classically (as is customary for the discussion of collision problems). An indication of how to deal with time-dependent fields is given in Chap. 7.

The simplest and best-studied systems are single atoms. Here a dynamical treatment is required only for the electrons (at least, as long as the atoms are not subject to electromagnetic fields): after transformation into the center-of-mass frame the Hamiltonian separates into a part governing the trivial translational motion of the complete atom and the motion of the electrons relative to the center-of-mass. As the