



# **Time-Dependent Density-Functional Theory**

*Concepts and Applications*

Carsten A. Ullrich

Time-dependent density-functional theory (TDDFT) describes the quantum dynamics of interacting electron many-body systems formally exactly and in a practical and efficient manner. TDDFT has become the leading method for calculating excitation energies and optical properties of large molecules, with accuracies that rival traditional wave function-based methods, but at a fraction of the computational cost.

This book is the first graduate-level text on the concepts and applications of TDDFT, including many examples and exercises, and extensive coverage of the literature.

The book begins with a self-contained review of ground-state DFT, followed by a detailed and pedagogical treatment of the formal framework of TDDFT. It explains how excitation energies can be calculated from linear-response TDDFT. Among the more advanced topics are time-dependent current-density-functional theory, orbital functionals, and many-body theory. Many applications are discussed, including molecular excitations, ultrafast and strong-field phenomena, excitons in solids, van der Waals interactions, nanoscale transport, and molecular dynamics.

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*Concepts and Applications*

Carsten A. Ullrich  
*University of Missouri*

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# Preface

Density-functional theory (DFT) is an enormously appealing method for determining the microscopic properties of matter. In quantum mechanics, the basic procedure is to start from Schrödinger's equation for the system of interest, be it an atom, a molecule, or a solid, and find the desired observables from the wave function. This is conceptually straightforward but becomes tedious as soon as there are more than just a few electrons. DFT instead proposes something radically different: forget about wave functions—the ground-state particle density, as shown by Hohenberg and Kohn in 1964, contains in principle enough information to determine all we need to know about any system. And it gets better: according to Kohn and Sham (1965), the density can be determined relatively easily by solving an effective one-particle problem!

But there is a price to be paid. The intricacies of the many-body problem are hidden away in the so-called exchange–correlation energy, which is a functional of the density (hence the name DFT). We don't know its exact form; approximations are unavoidable. Fortunately, the past decades have witnessed a steady stream of better and better exchange–correlation functionals, leading to more and more accurate results at low computational cost. This has fostered rapid growth in the popularity of DFT in physics, chemistry, materials science, biochemistry, and many other areas.

While DFT has been extremely successful for structural properties, there are many important issues which extend beyond its reach. Most notably, time-dependent processes and excited-state properties of electronic systems either are not included at all or are not easily accessible. This has motivated the development of time-dependent density-functional theory (TDDFT).

TDDFT is of relatively recent origin, dating back to the mid 1980s. It is an even stranger theory than DFT: the core idea is that the dynamics of any system of interacting fermions is completely encoded in its time-dependent density, which renders the wave function unnecessary. Again, the density can in principle be calculated relatively easily, but to do so, we need to deal with exchange–correlation effects that are even more involved than in the static case. In view of this, it almost borders on a miracle that we can actually find approximations that produce accurate results (and if they don't, that we can understand why).

Over the past few years there has been a flurry of activity in TDDFT, in particular when it became clear that this offers a superior alternative to traditional quantum chemistry methods for calculating optical excitation spectra of large molecules. The number of scientific publications using TDDFT methods continues to grow exponentially, with new applications in areas such as photosynthesis and photovoltaics, electronic transport through single molecules, ultrafast molecular dynamics, and laser control of chemical reactions. Over the past few years there have been several conferences, workshops, and schools dedicated solely to the subject of TDDFT.

All of this is evidence that TDDFT has become well defined as a subject on its own, with a growing community of scientists that constitutes a subset of the larger DFT community, yet has its own distinct character and speaks its own jargon. This book is a reflection of these exciting developments.

The purpose of this book is to provide readers at the graduate level with the necessary information and resources so they can learn TDDFT. But what does this mean? And what does one have to learn? That, of course, depends on one's particular needs. Everyday users of computer codes in quantum chemistry or materials science may encounter (TD)DFT only through menu options for the exchange-correlation functional. But it can take considerable experience to make a good choice: one needs to know how the various functionals perform compared with one another, and how to avoid potential pitfalls. Such experience is best gained by studying instructive examples. On the other hand, there is a smaller but very vibrant community of developers of TDDFT methodologies. For them, formal considerations, proofs, and technical details may be most important, but they should also know how the theory performs in practice.

In order to learn TDDFT, you first need to know DFT. This is a simple but somewhat loaded statement. Practically all TDDFT calculations start with a system in the ground state, which is prepared using DFT. Furthermore, many of the concepts and functionals of the time-dependent theory have been adapted from their static counterparts. This book therefore begins with an extensive and self-contained review of DFT.

However, it needs to be emphasized that TDDFT itself is much more than just an extension of DFT; the two theories are in fact *very different!* Just consider the existence proofs: in the time-dependent theory there is no minimum principle, and we have to worry about things like memory, causality, and initial states. On the practical level, both are highly interdisciplinary theories, with applications in physics, (bio)chemistry, materials science, and other areas. But DFT is concerned with structure, whereas TDDFT is concerned with dynamics.

Science books are often categorized either as textbooks or as monographs. The former are intended to teach the basics of a field to the newcomer. The latter are more specialized and mainly written for experts. In the end, this book has turned out to be a textbook *and* a monograph, and I hope I have succeeded in finding the right balance. I have tried to be as detailed and pedagogical as possible in the basic derivations and proofs, and to give many examples and exercises. Since TDDFT is such an interdisciplinary field, there are many special topics. They are introduced in such a way that little or no prior knowledge is required. But the book also contains over 800 references, and many additional resources in the appendices. As such, I believe that it captures the present state of the art in TDDFT.

I started this book in 2008, and have been working on it pretty much continuously over the past three years. It has grown to over 500 pages, since there was such a wealth of material to choose from—and, as every author knows, a book tends to take on a life on its own! To help readers find their way, Section 1.2 serves as a roadmap, in which I explain how the book is organized.

I have tried to do my best to cite the most relevant original references; limiting the selection was, of course, unavoidable. I apologize to all those authors whose work has

been omitted owing to an oversight of mine. Needless to say, typographical, mathematical, and other mistakes will be inevitable as well. Many of the most glaring errors and omissions were caught by colleagues and friends who were so kind as to serve as proof-readers. All the remaining mistakes are entirely my own. Corrigenda and addenda will be made available online at <http://www.missouri.edu/~mullrichc/tddft-book>.

I would like to acknowledge the hospitality of the Kavli Institute of Theoretical Physics at UC Santa Barbara, where parts of this book were written during a workshop in the fall of 2009. I also thank the University of Missouri-Columbia for granting me research leave during the 2009/2010 academic year.

There is a long list of colleagues and friends with whom I have interacted over many years, and I am deeply grateful for all their support and encouragement. In the first place, I would like to thank Neepu Maitra, Giovanni Vignale, Klaus Capelle, Stefano Pittalis, Oleg Vydrov, Robert van Leeuwen, and Suchi Guha for reading parts of the manuscript and making invaluable suggestions. I have profited from the knowledge and insight of many people in the (TD)DFI community and beyond. In particular, I wish to acknowledge many fruitful and enjoyable discussions with Kieror Burke, Philipp Jurek, Troy Van Voorhis, Angel Rubio, Walter Thiel, John Rehr, Claudia Ambrosch-Draxl, André Bandrauk, Massimiliano Di Ventra, Roberto D'Agosta, Heiko Appel, Ilya Tokatly, Paul De Bocij, Lucia Reining, and Irene D'Amico.

I also want to give credit to my past and current group members Harshani Wijewardane, Yonghui Li, Daniel Vieira, Ednilson Orestes, Fedir Kyrychenko, Volodymyr Turkowski, and Aritz Leonardo. This book is dedicated to all current and future students of TDDFT, in the hope that it will make a difference.

I feel incredibly fortunate that I was able to spend my years as a student and postdoc under the guidance and support of wonderful teachers and mentors: Hardy Gross, Paul-Gerhard Reinhard, Eric Suraud, Giovanni Vignale, Michael Flatté, and Walter Kohn. I would like to express my deepest gratitude to them.

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Columbia, May 2011

# Contents

<b>List of abbreviations</b>	xiii
<b>1 Introduction</b>	<b>1</b>
1.1 A survey of time-dependent phenomena	1
1.2 Preview of and guide to this book	7
<b>2 Review of ground-state density-functional theory</b>	<b>10</b>
2.1 The formal framework of DFT	11
2.2 Exact properties	21
2.3 Approximate functionals	30
PART I THE BASIC FORMALISM OF TDDFT	
<b>3 Fundamental existence theorems</b>	<b>45</b>
3.1 Time-dependent many-body systems	45
3.2 The Runge–Gross theorem	50
3.3 The van Leeuwen theorem	54
<b>4 The time-dependent Kohn–Sham scheme</b>	<b>59</b>
4.1 The time-dependent Kohn–Sham equation	59
4.2 Spin-dependent systems	61
4.3 The adiabatic approximation	62
4.4 The meaning of self-consistency in DFT and TDDFT	65
4.5 Numerical time propagation	67
<b>5 Time-dependent observables</b>	<b>73</b>
5.1 Explicit density functionals	73
5.2 Implicit density functionals	81
5.3 The time-dependent energy	88
<b>6 Properties of the time-dependent xc potential</b>	<b>91</b>
6.1 What is the universal xc functional?	91
6.2 Some exact conditions	93
6.3 Galilean invariance and the harmonic potential theorem	98
6.4 Memory and causality	103
6.5 Initial-state dependence	107
6.6 Time-dependent variational principles	111
6.7 Discontinuity upon change of particle number	115



<b>PART II LINEAR RESPONSE AND EXCITATION ENERGIES</b>	
<b>7</b>	<b>The formal framework of linear-response TDDFT</b> 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
<b>8</b>	<b>The frequency-dependent xc kernel</b> 157
8.1	Exact properties 157
8.2	Approximations 163
8.3	The xc kernels of the homogeneous electron liquid 164
<b>9</b>	<b>Applications to atomic and molecular systems</b> 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
<b>PART III FURTHER DEVELOPMENTS</b>	
<b>10</b>	<b>Time-dependent current-DFT</b> 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
<b>11</b>	<b>The time-dependent optimized effective potential</b> 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
<b>12</b>	<b>Extended systems</b> 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
<b>13</b>	<b>TDDFT and many-body theory</b> 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

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

<b>Appendix J</b>	<b>Constructing the scalar xc kernel from the tensor xc kernel</b>	455
<b>Appendix K</b>	<b>Semiconductor quantum wells</b>	458
K.1	Effective-mass approximation and subband levels	459
K.2	Intersubband dynamics	462
<b>Appendix L</b>	<b>TDDFT in a Lagrangian frame</b>	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
<b>Appendix M</b>	<b>Inversion of the dielectric matrix</b>	477
<b>Appendix N</b>	<b>Review literature on DFT and many-body theory</b>	479
<b>Appendix O</b>	<b>TDDFT computer codes</b>	482
<b>References</b>		484
<b>Index</b>		511

# List of abbreviations

Abbreviation	Meaning
1D, 2D, 3D	one, two, three dimensions (or -dimensional)
ACALDA	asymptotically corrected ALDA
ACFD	adiabatic-connection fluctuation-dissipation
ALDA	adiabatic local-density approximation
AOEP	adiabatic optimized effective potential
ATI	above-threshold ionization
RLYP	Roche-Lee Yang-Parr
BO	Born-Oppenheimer
BSE	Bethe-Salpeter equation
BZ	Brillouin zone
CAS	complete active space
CASPT2	complete active space with second-order perturbation theory
CB	Coulomb blockade
CC	coupled-cluster method
CC2	iterative second-order coupled-cluster method
CC3	iterative third-order coupled-cluster method
CCSDR(3)	coupled-cluster singles and doubles with noniterative triples correction method
CDFT	current-density-functional theory
CI	configuration interaction
CIS	configuration interaction singles
DFT	density-functional theory
EELS	electron energy loss spectroscopy
FSSH	fewest-switching surface hopping
GEA	gradient expansion approximation
GGA	generalized gradient approximation
GK	Gross-Kohn
HF	Hartree-Fock
HHG	high-harmonic generation

HOMO	highest occupied molecular orbital
IWHM	half-width at half-maximum
IXSS	inelastic X-ray scattering spectroscopy
KLI	Krieger-Li-Iafrate
LDA	local-density approximation
LR	long-range
LSDA	local-spin-density approximation
LUMO	lowest unoccupied molecular orbital
m.a.e.	mean absolute error
MP2	second-order Møller-Plesset perturbation theory
NCT	Nifosi-Conti-Tosi
NEGF	nonequilibrium Green's function
OEP	optimized effective potential
PBE	Perdew-Burke-Ernzerhof
PGG	Petersilka-Gossmann-Gross
QV	Qian-Vignale
RPA	random-phase approximation
SDFT	spin-density-functional theory
STC	self-interaction correction
SMA	small-matrix approximation
SPA	single-pole approximation
SR	short-range
TDA	Tamm-Dancoff approximation
TDCDFT	time-dependent current-density-functional theory
TDDFT	time-dependent density functional theory
TDELFF	time-dependent electron localization function
TDHF	time-dependent Hartree-Fock
TDKLI	time-dependent Krieger-Li-Iafrate
TDKS	time-dependent Kohn-Sham
TDOEP	time-dependent optimized effective potential
TDLDA	time-dependent local-density approximation
TDSDFT	time-dependent spin-density-functional theory
VK	Vignale-Kohn
xc	exchange-correlation

---

# 1

## Introduction

---

### 1.1 A survey of time-dependent phenomena

The world is constantly in motion. We perceive the flow of time by observing the occurrence of events in our everyday lives—the change of the seasons, the rising and setting of the sun, the motion of objects such as a falling stone, the ticking of a clock, our own heartbeat. Our natural senses allow us to experience changes with time on a scale ranging from a human lifetime down to fractions of a second. The lower limit of our reaction time is about a tenth of a second; this is why a movie requires at least 16 frames per second to appear continuous.

The physical and life sciences are concerned with the dynamics of time-dependent phenomena extending far beyond our immediate range of sensory perception. For example, geological and cosmological events unfold over very long times, sometimes billions of years. It would vastly exceed our patience (not to mention our lifespan) to try to directly observe such slow changes; one needs to rely on other, more indirect types of evidence.

The other extreme is processes taking place in the microscopic world, which are much too fast for us to see directly. However, we possess experimental technologies based on electronics and laser optics that allow us to achieve time resolution of microscopic events to within fractions of a femtosecond—over 15 orders of magnitude faster than the human eye can distinguish!

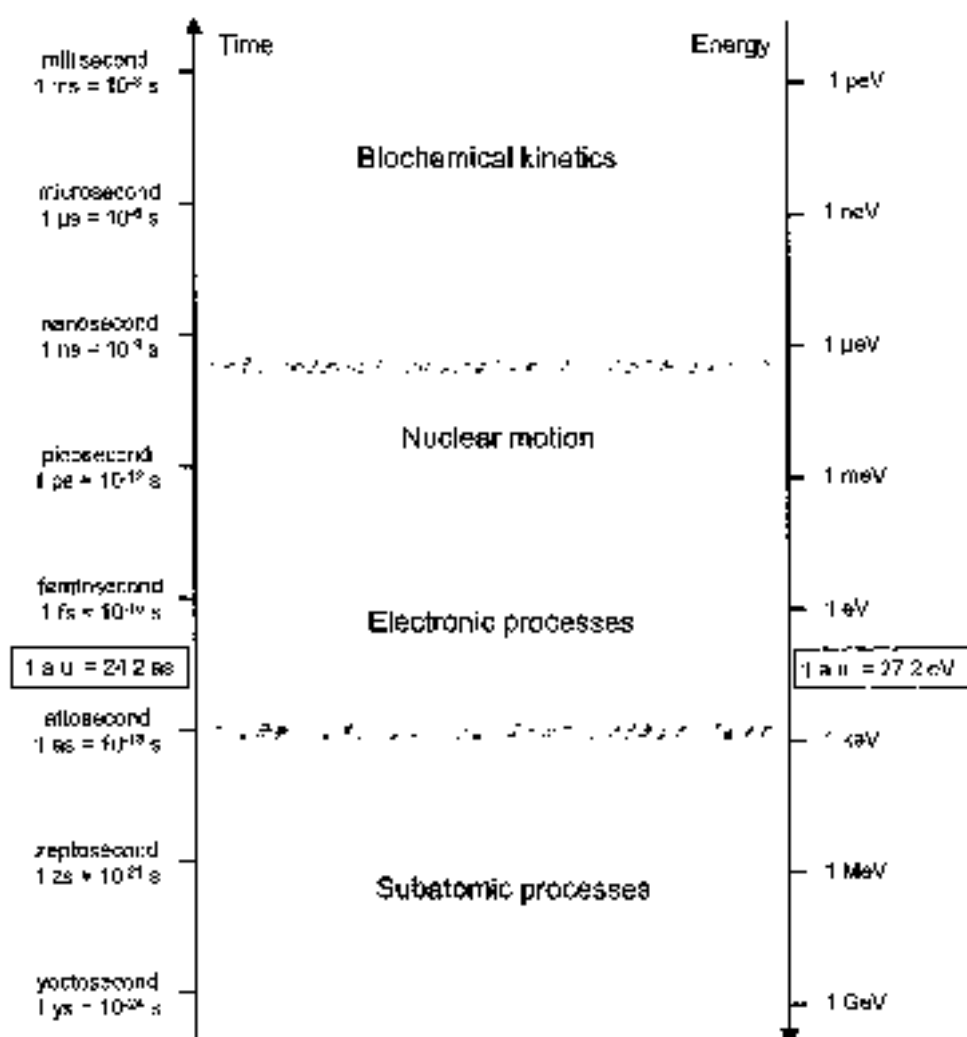
This book is about a theoretical and computational framework, time-dependent density-functional theory (TDDFT), whose purpose is the description and simulation of dynamical processes in quantum many-body systems. At the beginning, it is appropriate to mark the territory of TDDFT and discuss where this theory is expected to be applicable and practically useful. In this section, we will take a look at some of the physical processes occurring on very short timescales. This will set the stage for what is to follow in later chapters where the theory will be developed.

#### 1.1.1 A journey through 20 orders of magnitude

Time and energy are very closely related quantities. For instance, in the specific case of a monochromatic light wave, the energy of a photon is related to its frequency  $\nu$  and to its period  $T = 1/\nu$  via  $E = h\nu = h/T$ , where  $h$  is Planck's constant.

The most fundamental connection in quantum mechanics between time and energy arises through the time-energy uncertainty relation

$$\Delta t \Delta E \gtrsim \hbar, \quad (1.1)$$



**Fig. 1.1** Overview of time and energy scales, and associated characteristic processes in nature. An energy  $E$  on the right axis is related to a time  $t$  on the left axis via  $E = \hbar/t$ . The phenomena that TDDFT is concerned with—electronic processes and their coupling to nuclear motion—cover a range from about an attosecond to a few hundred picoseconds, as indicated by the wavy lines.

where  $\hbar = h/2\pi$ . The meaning of eqn (1.1) is that the uncertainty  $\Delta E$  in determining the energy of a system is inversely proportional to the time interval  $\Delta t$  that is available for doing the measurement.

Throughout this book, we will work in atomic units (a.u.); see Appendix A for an overview and precise definitions. The atomic units of time and of energy are 24.2 attoseconds and 27.2 eV, respectively.

Figure 1.1 gives a general overview of the relevant timescales for “fast” processes occurring in nature, spanning over 20 orders of magnitude. Figure 1.1 is divided into four regions: subatomic processes, electronic processes, nuclear motion, and biochemical kinetics. Let us now take a closer look at each region.

*The subatomic region.* The first region, subatomic processes, extends from the sub-attosecond/MeV scale all the way down, in principle, to the Planck time and energy.<sup>1</sup> This includes the dynamics of nuclear excitation and collision processes and the lifetimes of elementary particles. Modern particle accelerators such as the Large Hadron Collider (LHC) at CERN in Geneva are designed to explore new physics (beyond the standard model of particle physics) occurring at energies up to several TeV, which corresponds to sub-ys timescales. The area of high-energy physics is beyond the scope of TDDFT.

*The electronic region.* TDDFT is mainly concerned with electronic excitation processes and the associated time evolution in atoms, molecules, and condensed-matter systems away from equilibrium. On a fundamental level, these processes are described by the (nonrelativistic) time-dependent Schrödinger equation; as we will see, TDDFT provides a formally exact and practically useful alternative to the full many-body Schrödinger equation.

The electronic phenomena that we will be interested in take place in a time window from about an attosecond to a few hundred picoseconds, with corresponding energies ranging from  $\mu\text{eV}$  to keV. Inner-shell electronic excitations by X-rays in atoms and molecules can happen very fast, on an attosecond timescale; other types of electronic excitation processes in larger systems (for example, collective plasma oscillations) may take more time, typically in the range of 10–100 fs.

*The nuclear-motion region.* Atomic nuclei are several thousand times more massive than electrons, and therefore move more slowly. The vibrations in a molecule have periods of the order of picoseconds. The motion of the nuclei dictates the formation or breaking of bonds, the rearrangement of functional groups in a molecule, and generally how long it takes for chemical reactions to occur. Such processes can last over hundreds of picoseconds, depending on the size and complexity of the system.

The motion of the nuclei in molecules and solids is formally described by a coupled Schrödinger equation for the electronic and nuclear degrees of freedom. Such calculations are only feasible for very small systems. In practice, the nuclear degrees of freedom are often treated classically, while the electron dynamics is treated fully quantum mechanically.

*The biochemical region.* We leave the domain of TDDFT when we consider phenomena that are even slower than the above processes, i.e., taking longer than a nanosecond, ranging up to milliseconds. This is the regime in which chemical and biological kinetics take place: chemical reactions involving complex molecules, certain catalytic processes, enzymatic reactions, and protein folding. Another ubiquitous phenomenon in this regime is the Brownian motion of small particles. The dynamics of

<sup>1</sup>The shortest meaningful time interval in nature is known as the Planck time; it is defined as  $t_P = \sqrt{\hbar G/c^5} = 5 \times 10^{-44}$  s, where  $G$  is the gravitational constant and  $c$  is the speed of light. The corresponding Planck energy, defined as  $E_P = \hbar/t_P$ , is about  $10^{19}$  GeV. At such unimaginably short timescales our concept of a space and time continuum breaks down, and quantum theory and gravitation are thought to merge. This regime, which is still subject to much speculation, is over 20 orders of magnitude beyond the time and energy scales discussed in this book.



such processes is strongly influenced by statistical and thermal fluctuations. Powerful theoretical simulation tools are available in the form of molecular dynamics with classical force fields.

### 1.1.2 What do we want to describe?

A common starting point for discussing the properties of matter is a characterization of the ground or equilibrium state. For a system consisting of electrons and nuclei, this means that we want to determine quantities such as total ground-state energies, electronic density distributions, equilibrium geometries, bond lengths and bond angles, lattice constants, forces and elastic constants, dipole moments and static polarizabilities, and magnetic moments. These tasks can be achieved with ground-state DFT.

TDDFT allows us to describe the behavior of quantum systems that are not in the ground state or in an equilibrium state. Although this can mean many different things, we can define three typical, generic scenarios:

- A system—say, an atom or a molecule—is initially in its ground state. At some time, we act on it with an external perturbing force and watch what happens. The perturbation can be a short one, such as a femtosecond laser pulse or a collision with a fast projectile, or it can be a steady one, such as a continuous laser field. What we are interested in is the *dynamical response* of the system to the perturbation.
- At the initial time, the system finds itself in a nonequilibrium state, i.e., it is not in an eigenstate. We leave the system to itself and observe how it freely evolves in time. Typical examples are the motion and spreading of a wave packet, and the collective plasma oscillations of the conduction electrons in a metal.
- The system is in one of its electronic excited states. Since these are quantum mechanical eigenstates of the Hamiltonian, the system is stationary. Obtaining excited-state properties such as energies, geometries, or forces is one of the main areas in which TDDFT is used.<sup>2</sup>

TDDFT is very closely related to various types of *spectroscopy*. In general, carrying out a spectroscopic measurement means that the system of interest is subject to some probe—a laser field, a beam of particles, or a static or time-varying electric or magnetic field. The probe triggers some form of change in the sample, such as electronic transitions, currents, induced dipoles, or ionization. These changes in the sample are measured and analyzed by a detector, which then tells us something about the related spectral properties of the system.

There are a vast number of different spectroscopic techniques, and we will encounter a few of them in this book. One distinguishes *linear* from *nonlinear* spectroscopy. “Linear” here means that one is interested in that part of the response of the system which is proportional to the strength of the perturbation. The theoretical counterpart of this is *linear-response theory*. As we will see, most applications of TDDFT today are in this regime. But TDDFT is also applicable in the nonlinear regime, where the external perturbation is strong.

<sup>2</sup>Some of these excited-state properties can, in principle, also be obtained from DFT, but this is much more subtle and difficult to do in practice than using TDDFT. See also Appendix F.

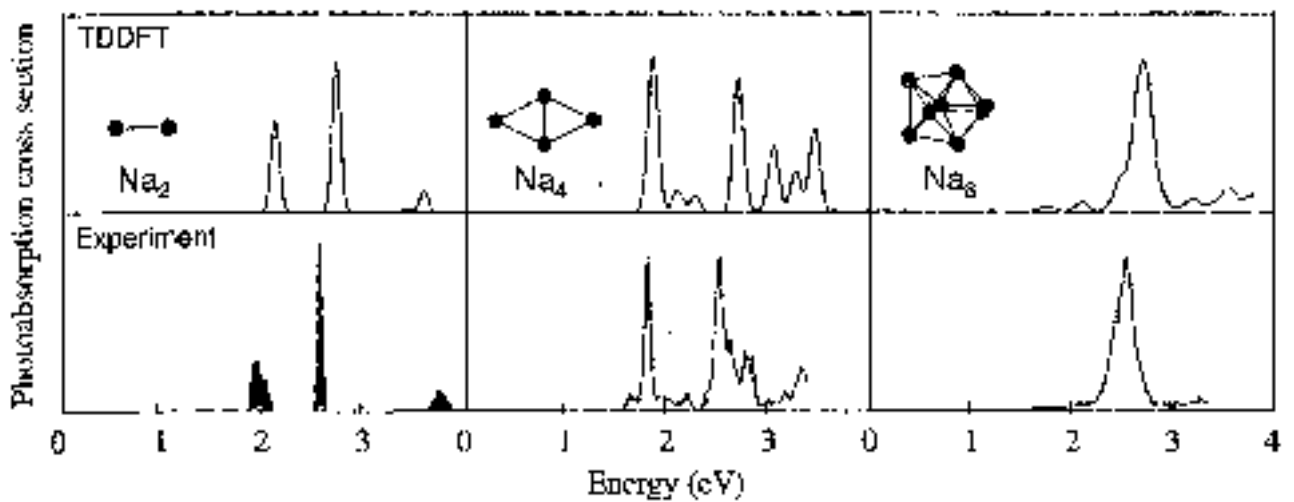


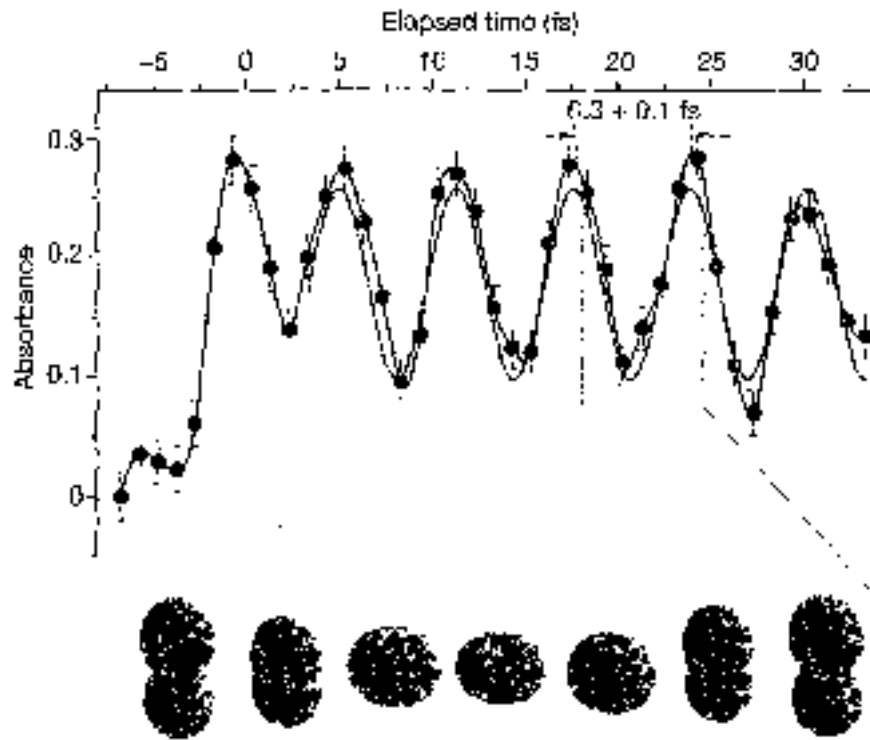
Fig. 1.2 Photoabsorption spectra of small Na molecules, comparing TDDFT calculations with experimental data. [Adapted with permission from APS from Vasiliev *et al.* (2002), ©2002.]

A typical example of linear spectroscopy is given in Fig. 1.2. The figure shows results from a photoabsorption measurement on small Na molecules. The position of each peak corresponds to an electronic excitation induced in the molecule; the peak height is proportional to the so-called oscillator strength, which is a measure of the efficiency with which that particular transition couples to the light at that frequency. The measured spectra are very well reproduced by TDDFT.

This example shows that TDDFT can be very useful for calculating electronic excitations and related optical properties of molecules. In this book we will learn the details of how this is done. Nowadays, TDDFT is used to describe excited-state properties of molecules with hundreds of atoms. We will pay particular attention to identifying “difficult” cases (for instance, so-called charge-transfer excitations), and will discuss what the challenges are and how to handle them.

Photoabsorption spectra such as those in Fig. 1.2 are measured by exposing the system to a continuous optical driving field; the response is in the form of steadily oscillating dipole signals, which are then Fourier-transformed to generate a spectrum. Often, however, one is interested in the fast response of a system, triggered by very short, pulsed excitations. The standard technique to measure real-time dynamics is through *pump-probe* techniques. The “pump” pulse sets off some dynamical behavior in the system, and the “probe” pulse examines it after some time delay.

An example of a pump-probe experiment to reveal the real-time motion of valence electrons in a Kr ion is shown in Fig. 1.3 (Goulielmakis *et al.*, 2010). In the first stage of the experiment, Kr atoms are ionized using few-cycle laser pulses of sub-4 fs duration and a wavelength of 750 nm. An electron is quickly removed from the  $4p$  shell; the remaining  $\text{Kr}^+$  ion finds itself in a coherent superposition of two states separated by spin-orbit splitting,  $4p_{3/2}^1$  and  $4p_{1/2}^1$ . The associated “hole” in the valence shell pulsates with a frequency inversely proportional to this splitting. Using probe pulses with a duration of less than 150 as, this pulsating motion is “strobed” in real time. The reconstructed wave-packet motion is shown in Fig. 1.3.



**Fig. 1.3** Reconstruction of the valence-shell electron wave-packet motion of a Kr ion, measured in an attosecond pump-probe experiment. Top: time-resolved absorbance, averaged over the photon energy range 81.30–81.45 eV, corresponding to the  $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$  transition. Bottom: ensemble-averaged hole density distributions in the  $4p$  subshell of  $\text{Kr}^+$ , at instants separated by 1 fs, within an interval of 17–25 fs following ionization. [Adapted with permission from Macmillan Publishers Ltd from Goulielmakis *et al.* (2010), ©2010.]

TDDFT is suitable for real-time simulations of the electron dynamics following ultrafast, short-pulse excitations.<sup>3</sup> It can describe the attosecond density fluctuations following the removal of inner-shell electrons (Breidbach and Cederbaum, 2005), and it can simulate how an atom ionizes over a duration of tens of femtoseconds by emitting packets of density (see Fig. 1.4). TDDFT can also be used to describe the coupled electron–nuclear dynamics of an excited molecule, including dissociation and fragmentation processes.

To conclude this brief survey of the time-dependent phenomena which will be of interest in this book, let us look at a different type of nonequilibrium situation. Figure 1.5 shows the transport characteristics of an *A*-DNA strand which is attached to gold electrodes via thiol linkers and subject to a range of bias voltages. The current–voltage ( $I$ – $V$ ) curve indicates very low currents for small bias voltages, as long as the Fermi levels of the left and right leads are in the HOMO–LUMO gap<sup>4</sup> of the molecule. The  $I$ – $V$  curve is asymmetric about zero bias because the molecule has a native dipole moment.

<sup>3</sup>The experiment shown in Fig. 1.3 involves states separated by spin-orbit splitting. Such fine-structure effects are not contained within standard (nonrelativistic) TDDFT.

<sup>4</sup>The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).



**Fig. 1.4** Schematic illustration of density fluctuations, deformations, and ionization of an atom hit by an intense laser pulse. The right figure is a snapshot of the highly excited atom, which emits packets of electronic density into the continuum. Processes such as this typically take place within a few tens of femtoseconds.

The steady-state transport through a molecular junction, as studied in Fig. 1.5, does not appear to be a time-dependent phenomenon at first glance. Nevertheless, treating it with ground-state methodologies such as static DFT would be incorrect, since it represents a nonequilibrium situation with a steady current between two infinite reservoirs.

## 1.2 Preview of and guide to this book

This book gives an introduction to TDDFT for the newcomer, as well as an overview of the state of the art in the field for more advanced readers. We will discuss the formal framework of TDDFT and a broad spectrum of applications.

We begin with a self-contained review of ground-state DFT in Chapter 2. This review covers the basic formalism such as the Hohenberg–Kohn theorem, constrained search, and the Kohn–Sham equations. An extensive overview of the most popular approximate exchange–correlation functionals is given and illustrated with some results. Readers familiar with static DFT can skip this chapter, but we refer back later to it in many places.

The remainder of the book is divided into four parts.

*Part I: the basic formalism of TDDFT.* In Chapter 3, the basic existence theorems of TDDFT will be introduced, with detailed proofs of the Runge–Gross and van Leeuwen theorems. The remaining chapters, Chapters 4, 5, and 6, then focus on the time-dependent Kohn–Sham approach. We will explain how the time-dependent Kohn–Sham equations can be solved, and what kind of observables can be obtained from the time-dependent density. The key quantity in TDDFT, the time-dependent exchange–correlation (xc) potential, is the subject of Chapter 6; a long list of its exact properties will be discussed.

*Part II: linear response and excitation energies.* The majority of applications of TDDFT are to the calculation of excitation energies of molecular systems. In Part II of this book, we explain how this is done. Chapter 7 contains the necessary formalism: it begins with a summary of linear-response theory, and shows how the frequency-dependent linear density response can be calculated exactly, in principle, with TDDFT.

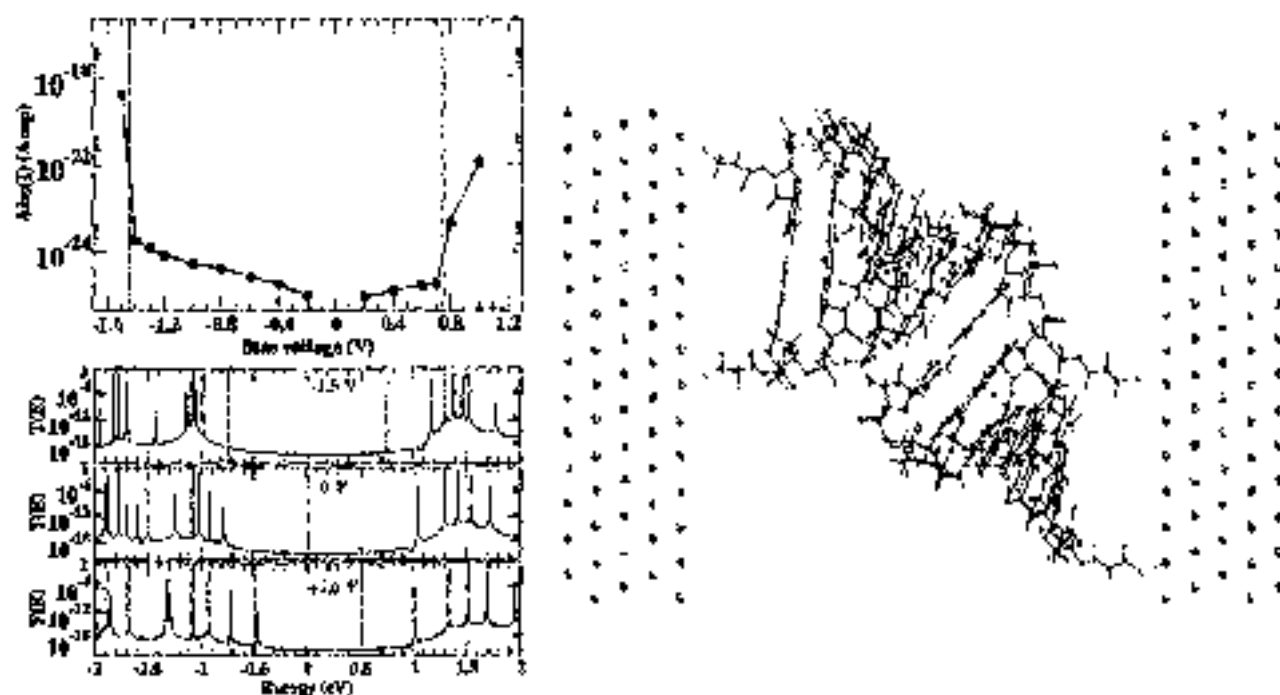


Fig. 1.5 Transport characteristics of a G5'G3' A-DNA strand between gold electrodes, calculated using TDDFT. Left, top:  $I$ - $V$  curves. Left, bottom: transmission coefficients as a function of energy at different bias voltages. The vertical dashed lines mark the bias windows. [Adapted with permission from APS from Pemmaraju *et al.* (2010), ©2010.]

From this, we show how excitation energies can be calculated using the Casida equation.

Chapter 8 is concerned with the key quantity of linear-response TDDFT, the so-called  $\kappa$  kernel. We discuss its properties and present some approximations, in particular for the homogeneous electron liquid. Chapter 9 is an extensive review of the performance of TDDFT for excitations in atomic and molecular systems. We cover “mainstream” applications where TDDFT has been very successful, but also more challenging problems such as double excitations and charge-transfer excitations.

*Part III: further developments.* The development of accurate exchange–correlation functionals is a key task in TDDFT, and in Chapters 10–13 we present several methods to do this. Chapter 10 contains a thorough treatment of time-dependent current-DFT, placing particular emphasis on the development of nonadiabatic (i.e., memory-dependent) functionals and the description of dissipation. In Chapter 11 we introduce the optimized-effective-potential method, which is a formally rigorous way of dealing with orbital-dependent  $\kappa$  functionals. As we will see, orbital functionals offer a road towards the systematic construction of improved functionals, starting from the exchange-only limit.

Excitations and optical properties of extended solids are the subject of Chapter 12. We distinguish between metallic systems, where the dominating excitations have a collective, plasmon-like nature, and insulators, where excitonic effects are important. Finally, in Chapter 13 we discuss several approaches to the systematic construction of  $\kappa$  functionals based on many-body theory.

**Part IV: special topics.** In this part, we discuss various applications of TDDFT to “special” situations: long range correlations and van der Waals interactions (Chapter 14), nanoscale transport and molecular junctions (Chapter 15), strong-field phenomena and optimal control (Chapter 16), and excited-state potential energy surfaces and molecular dynamics (Chapter 17). Each chapter is self-contained and requires essentially no previous knowledge of the topic. The goal is to illustrate the breadth of TDDFT, and how it provides an attractive alternative to “traditional” approaches in many different areas.

### 1.2.1 Prerequisites and other remarks

This book addresses a diverse readership in theoretical and computational (bio)chemistry, condensed-matter physics, materials science, and other areas where time- and frequency-dependent electronic processes are of interest. The prerequisite is a basic knowledge of quantum mechanics at the beginning graduate level. The book is written in first quantization throughout, except for some passages in Chapter 13 where second quantization is introduced in a rather informal manner.

Our treatment of many-body theory (Green’s functions and Feynman diagrams) is far from rigorous, but is intended to be as easy and accessible as possible, and just detailed enough for nonexpert readers to be able to appreciate the connection with TDDFT. Thus, prior knowledge of many-body theory is certainly helpful, but not required. An extensive literature list is given in Appendix N.

Every chapter (except this one) contains a number of exercises. This book should therefore be suitable as a textbook or as supplementary material for a graduate level course on (TD)DFT, electronic-structure theory, computational chemistry or materials science, or other related topics. Many of the chapters (especially in Part IV) are quite self-contained and can be studied rather independently of one another. On the other hand, this book is strongly interconnected, and the reader will discover many links and cross-references to earlier and later chapters.

The most effective way of learning a subject, in addition to studying the theoretical aspects, is through hands-on activities. There are several numerical exercises in this book; a few of them involve some programming. Appendix O lists a number of computer codes that have TDDFT options, including a long list of open-source codes. Adventurous readers are encouraged to install these codes and start their own explorations.

# Review of ground-state density-functional theory

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Before we begin discussing the formal and practical aspects of time-dependent density-functional theory, it is an essential prerequisite to review the basic concepts of ground-state density-functional theory (DFT). Today, DFT is widely accepted as a universal approach to electronic-structure calculations, and it is being used by tens of thousands of researchers worldwide, working in areas as diverse as drug design, metallurgy, nanotechnology, geology, and astrophysics, to name just a few. In this chapter we explain in a nutshell what DFT is, how it works, and why it is so popular.

There are several reasons why a solid grasp of the basics of DFT is necessary before one begins to study TDDFT:

- Many of the essential concepts and practical ingredients of TDDFT—such as the time-dependent Kohn–Sham equations, and approximations to the exchange–correlation potential—have their counterparts in static DFT and make use of similar ideas.
- A standard scenario in TDDFT is to begin with a system in its ground state, which is then acted upon by a time-dependent perturbation. The initial state needs to be calculated with DFT before one can start using TDDFT.
- There is a well-defined static limit in which TDDFT reduces to DFT, namely, when a system is initially in its ground state and there is no perturbation: the system is just sitting there and doing nothing. This case may sound trivial, but it is a very important check of the consistency of the time-dependent theory.

The purpose of the present chapter is to provide the “bare essentials” which are needed as part of the foundation upon which TDDFT is built. We will therefore discuss the basic formal framework of DFT, go over the various approximations to the exchange–correlation (xc) functionals that are in use today, and review some of the most important exact properties, practical aspects, and applications of the theory.

Needless to say, it is impossible to squeeze the vast amount of knowledge in the area of DFT accumulated over the years into a single introductory chapter. There exists a large body of literature on the subject of DFT; some of the most popular review articles and textbooks are listed in Appendix N. The interested reader is encouraged to consult these to gain a more comprehensive overview of the history and the current state of the art of this vibrant and diverse field of research.

## 2.1 The formal framework of DFT

### 2.1.1 The electronic many-body problem

DFT is a formally exact approach to the static electronic many-body problem. What do we mean by this? In this section, we define the electronic many-body problem to consist in finding the solutions of the static Schrödinger equation for a system of  $N$  interacting nonrelativistic electrons.

$$\hat{H}\Psi_j(\mathbf{x}_1, \dots, \mathbf{x}_N) = E_j\Psi_j(\mathbf{x}_1, \dots, \mathbf{x}_N). \quad (2.1)$$

Here, the antisymmetric  $N$ -electron wave function  $\Psi_j(\mathbf{x}_1, \dots, \mathbf{x}_N)$  is the  $j$ th eigenstate of the Hamiltonian  $\hat{H}$ , with associated energy eigenvalue  $E_j$ . We use  $\mathbf{x}_j \equiv (\mathbf{r}_j, \sigma_j)$  as a shorthand notation for the space and spin coordinates of the  $j$ th electron. In the following, we shall not explicitly indicate the arguments  $\mathbf{x}_1, \dots, \mathbf{x}_N$  of an  $N$ -electron wave function, unless needed.

The total Hamiltonian of the  $N$ -electron system is given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}, \quad (2.2)$$

where the kinetic-energy operator is

$$\hat{T} = \sum_{j=1}^N \frac{\nabla_j^2}{2} \quad (2.3)$$

( $\nabla_j$  denotes the gradient operator with respect to  $\mathbf{r}_j$ , the position vector of the  $j$ th electron), the potential operator is

$$\hat{V} = \sum_{j=1}^N v(\mathbf{r}_j), \quad (2.4)$$

and the electron–electron interaction is in general

$$\hat{W} = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}}^N w(|\mathbf{r}_j - \mathbf{r}_k|). \quad (2.5)$$

The usual choice is of course the Coulomb interaction  $w(|\mathbf{r}_j - \mathbf{r}_k|) = 1/|\mathbf{r}_j - \mathbf{r}_k|$ , but different forms of the interaction, including zero interaction, are also allowed.

Notice that eqn (2.1) is the Schrödinger equation for the electronic degrees of freedom only. A more general formulation of the structure of matter would also include the nuclear degrees of freedom on an equal footing; here, we treat all nuclei as fixed and producing a given Coulomb potential, which contributes to the total external potential  $v(\mathbf{r})$ . This is known as the Born–Oppenheimer approximation. In Chapter 17 we will give a precise definition of the Born–Oppenheimer approximation, and we will also discuss approaches to the coupling of electronic and nuclear dynamics.



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