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 ν 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

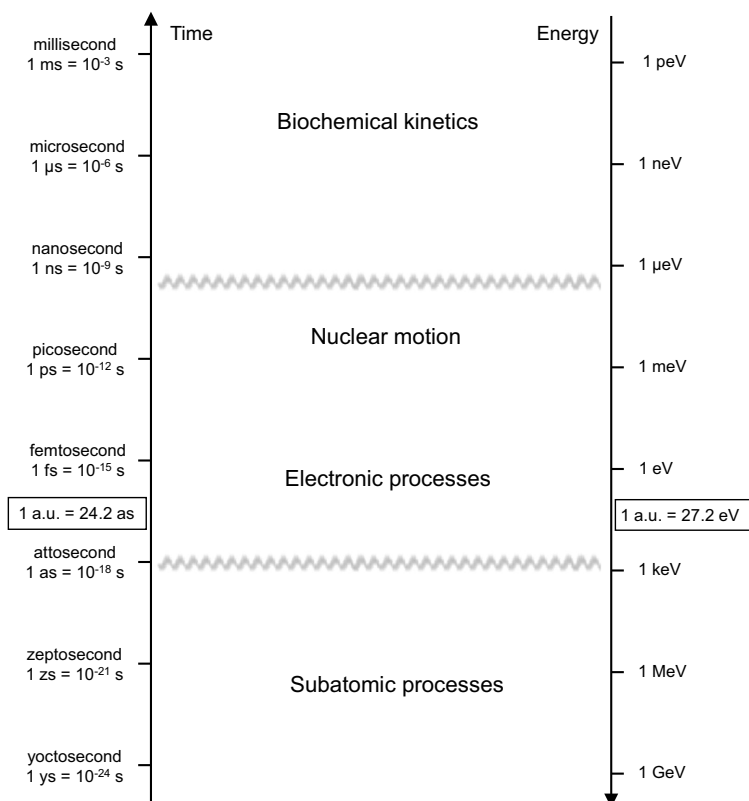$$\Delta t \, \Delta E \gtrsim \hbar \,, \tag{1.1}$$

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 ΔE in determining the energy of a system is inversely proportional to the time interval Δt 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.[1] 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 µeV 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

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[1]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.[2]

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.

[2]Some of these excited-state properties can, in principle, also be obtained from DFT, but this is much more subtle and difficult do to in practice than using TDDFT. See also Appendix F.
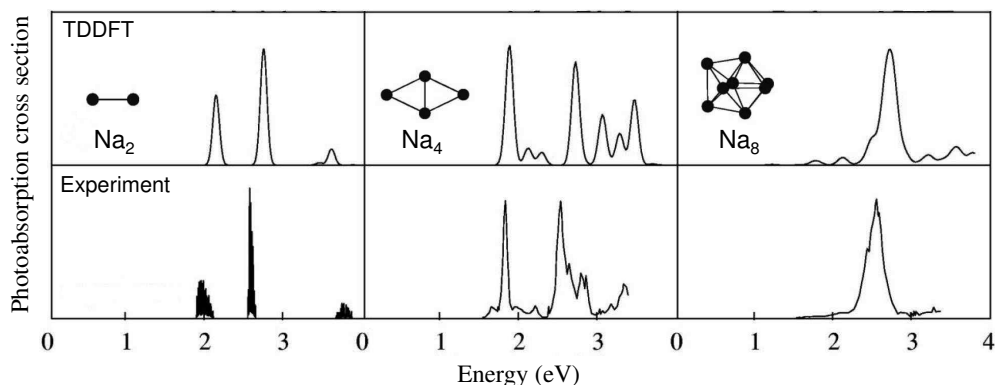
Fig. 1.2 Photoabsorption spectra of small Na molecules, comparing TDDFT calculations with experimental data. [Adapted with permission from APS from Vasiliev *et al.* (2002), ©2002.]

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 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.
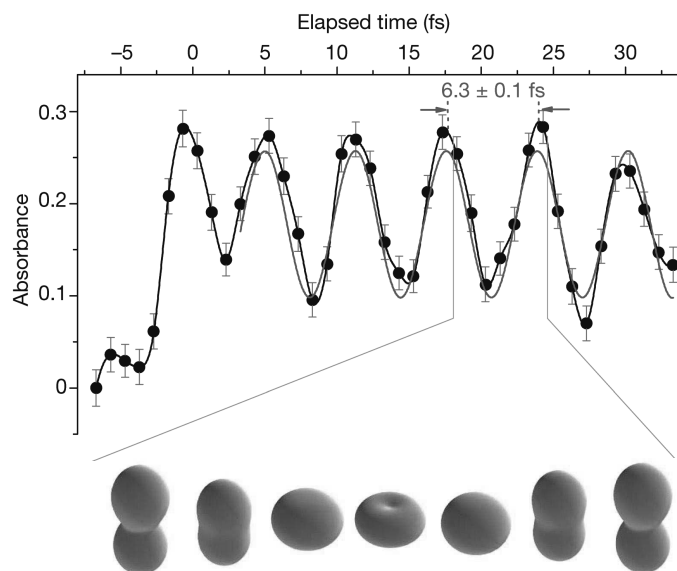
Fig. 1.3 Reconstruction of the valence-shell electron wave-packet motion of a Kr ion, measured in an attosecond pump–probe experiment. Top: time-resolved absorbance, averaged over the photon energy range 81.20–81.45 eV, corresponding to the $4p_{3/2}^{-1} \to 3d_{3/2}^{-1}$ transition. Bottom: ensemble-averaged hole density distributions in the $4p$ subshell of 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.[3] 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[4] of the molecule. The *I*–*V* curve is asymmetric about zero bias because the molecule has a native dipole moment.

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[3]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.

[4]The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).
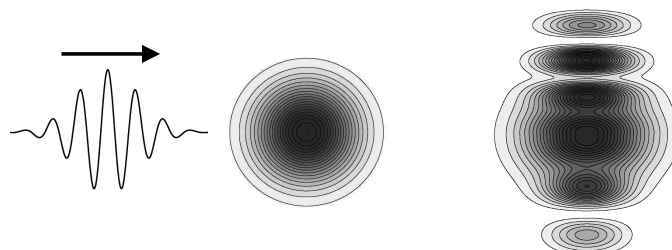
Fig. 1.4 Schematic illustration of density fluctuations, deformations, and ionization of an atom hit by an intense laser pulse. The right figure is a snapshot of the highly excited atom, which emits packets of electronic density into the continuum. Processes such as this typically take place within a 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.
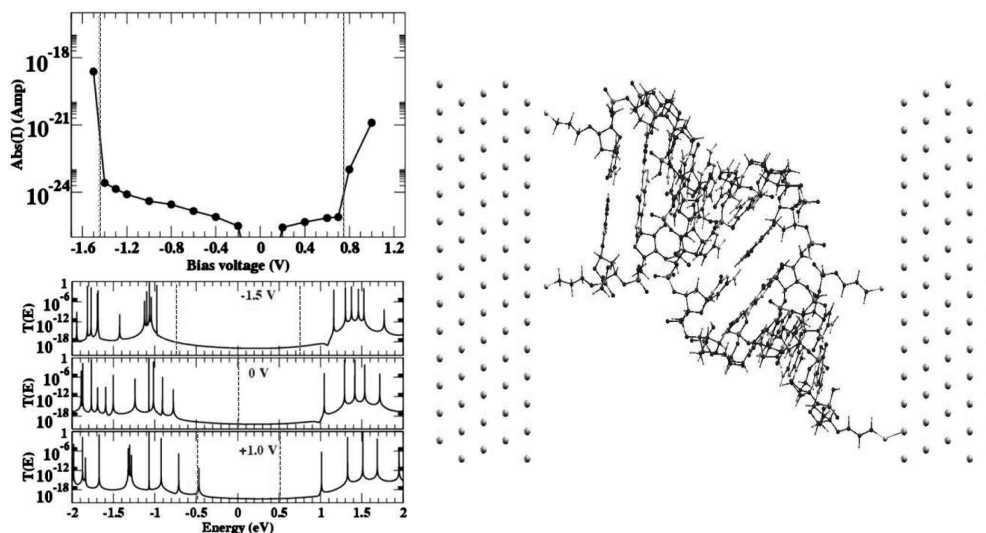
Fig. 1.5 Transport characteristics of a G5′G3′ *A*-DNA strand between gold electrodes, calculated using TDDFT. Left, top: *I–V* curve. Left, bottom: transmission coefficients as a function of energy at different bias voltages. The vertical dashed lines mark the bias windows. [Adapted with permission from APS from Pemmeraju *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 xc 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 xc 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 xc 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.