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Introduction

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On dynamics

Remarkable progress has been made in the elucidation of ultrafast dynamics and its control driven by femtosecond laser pulses in small molecules, large-scale molecular systems, clusters, nanostructures, surfaces, condensed phase and biomolecules. The exploration of photoinduced ultrafast response, dynamics, reactivity and function in ubiquitous molecular, nanoscale, macroscopic and biological systems pertains to the interrogation and control of the phenomena of energy acquisition, storage and disposal, as explored from the microscopic point of view. Photoinduced ultrafast processes in chemistry, physics, material science, nanoscience, and biology constitute a broad, interdisciplinary, novel and fascinating research area, blending theoretical concepts and experimental techniques in a wide range of scientific disciplines. The foundations for the analysis and control of ultrafast photoinduced processes were laid during the last eighty years with the development of nonradiative dynamics from small molecules to biomolecules [1–6], while during the last twenty years remarkable progress was made with the advent of femtosecond dynamics and control at the temporal resolution of nuclear motion [1, 7–12]. This scientific historical development can be artistically described by ascending the 'magic mountain' of molecular, cluster, condensed phase and biological dynamics by several paths (Fig. 1.1), all of which go heavenwards toward a unified and complete description of structure-electronic level structure-spectroscopy-dynamics-function relations and correlations.

The genesis of intramolecular nonradiative dynamics dates back to the origins of quantum mechanics, when the 1926 groundbreaking work of Schrödinger and Heisenberg laid the foundations for the description of time-dependent phenomena in the quantum world. In 1928 Bonhoeffer and Farkas [13] observed that predissociation in the electronically excited ammonia molecule, which involves the decay of a metastable state to a dissociative continuum, i.e., $\mathrm{NH_3} \xrightarrow{h\nu} \mathrm{NH_3^*} \xrightarrow{1/\tau} \mathrm{NH_2 + H}$, is manifested by spectral line broadening, with
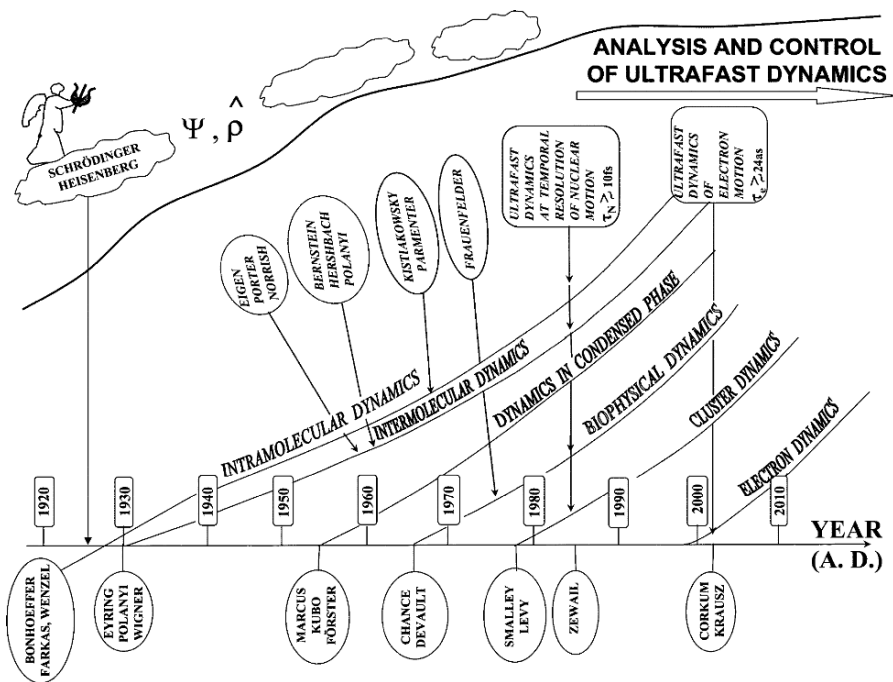
Fig. 1.1. An artist's view of the 'magic mountain' of the evolution of dynamics. The names of some of the pioneers who initiated each scientific area are marked on the paths.

a spectral linewidth Γ that considerably exceeds the radiative linewidth. This seminal work established the first spectroscopic-dynamic relation, providing experimental verification of the Heisenberg energy-time uncertainty relation, and pioneering the field of intramolecular dynamics. At about the same time, Wenzel [14] worked on another facet of nonradiative dynamics for the theory of atomic autoionization, establishing the basic unified theory of nonradiative processes. For a metastable (predissociating or autoionizing) state into a (dissociative or ionization) continuum, the decay lifetime τ was quantified in terms of the Golden Rule $\tau^{-1} = (2\pi/\hbar)|V|^2(dn/dE)$, where V is the matrix element of the Hamiltonian inducing the nonradiative transition, and dn/dE is the density of states. The Golden Rule played a central role in providing a conceptual basis for intramolecular dynamics from reactive processes in diatomics to radiationless transitions in 'isolated' large molecules. In 1931 Eyring and Polanyi [15] constructed the first potential energy surface for chemical reactions, a concept with continuous impact on the field. In the context of the present book it is noteworthy to point out that both studies of Bonhoeffer and Farkas [13] and of Eyring and Polanyi [15] were conducted in Berlin-Dahlem, the location of the Sfb 450 research center, (see below). Further important

developments in the realm of intermolecular dynamics were pioneered in the 1930s by Eyring, Polanyi, and Wigner, with remarkable evolution in the 1970s for collision dynamics in molecular beams [16]. Subsequently, experiment and theory moved toward the realm of large, complex systems. A distinct field of dynamics in the condensed phase was pioneered in the 1950s by Marcus [17], Förster [18], and Kubo [19]. Marcus [17] advanced the cornerstone of the electron transfer theory in solution in terms of the Gaussian free energy (ΔE) relation for the rate $k \propto \exp[-(\Delta E + \lambda)^2/4\lambda k_B T]$ (where λ is the medium reorganization energy), leading to central kinetic and spectroscopic results for correlation rules, free-energy relations, uniqueness of the inverted region and charge transfer spectroscopy. Conceptually and physically isomorphic classes of condensed phase dynamics pertain to the Förster theory of electronic energy transfer [18]. At the same time, Kubo and Toyozawa [19] developed the theory of electron-hole recombination in semiconductors, which bears analogy to electron transfer, although at that time the interrelationship between their work and the Marcus theory was not realized. The extension of dynamics to the protein medium emerged in the 1960s with the development of biophysical electron transfer dynamics, with experimental and theoretical studies of charge separation in photosynthesis [20]. In 1975 further progress by Fraunfelder [21] in biophysical dynamics led to the description of the energy landscapes of proteins. Concurrently, progress was made in the dynamics of large-scale chemical systems. In 1965 Kistiakowsky and Parmenter [22] observed intersystem crossing within the benzene molecule in the low-pressure gas phase, stating that 'a strictly intermolecular nonradiative transition is difficult to reconcile with concepts of quantum mechanics' [22]. Three years later the theory of intramolecular radiationless transitions in 'isolated' molecules was developed [23]. In 1969, the theory of time-dependent coherence phenomena in large molecules was advanced [24] providing the conceptual basis for molecular wave packet dynamics. The conceptual framework for intramolecular radiationless transitions and coherence effects encompassed both interstate dynamics involving internal conversion, a well as intersystem crossing, and intrastate dynamics involving vibrational energy redistribution. In the 1970s, the practice and concepts of dynamics moved toward large finite systems. Cluster dynamics, which constituted the border line between molecular and condensed phase phenomena, emerged with the work of Smalley, Wharton and Levy [25] on the vibrational predissociation of HeI$_2$ clusters. Cluster dynamics built bridges to the response, dynamics, reactivity and structure of large finite systems [26–28], i.e., size-selected clusters [29], superfluid quantum clusters and nanodroplets [30], finite ultracold gases (temperatures of 100μK-10nK) [31] and nanostructures [32]. Some fascinating dynamic processes involve resonant and dissipative vibrational energy flow and intramolecular vibrational energy distribution in clusters [33], selective, size dependent reactivity and microscopic catalysis on metal clusters [27,28], Coulomb instability leading to fission or Coulomb explosion of multicharged elemental, molecular and metal clusters [34, 36], the expansion of optical molasses that are

isomorphic to cluster Coulomb explosion [31], as well as transport of elementary excitations in nanostructures [35] that opens avenues for molecular- and nano-electronics [35].

Since 1985 the exploration of ultrafast chemical and biological dynamics stemmed from concurrent progress in experiment and theory. The advent of femtosecond dynamics by Zewail in 1987 [37–39] allowed for the exploration of dynamics in molecules, clusters, condensed phase, surfaces and biomolecules on time scales for intramolecular motion (10-100fs) and for intermolecular motion (100fs-1ps) [1, 7–9, 11]. Notable novel phenomena pertained to radiationless transition, wave packet dynamics, coherence effects, transition-state spectroscopy, cluster dynamic size effects, nonadiabatic condensed phase dynamics, ultrafast electron and proton transfer, charge separation in photosynthesis, and nonlinear optical interactions [1,7–9,11,40–45]. Recent advances in the elucidation of structure-dynamics-function relations in molecules, clusters, nanostructures, surfaces, and biomolecules are described in this book.

The interrogation and analysis of dynamics at the temporal resolution of nuclear motion raised important issues regarding the manipulation of the optical properties, response, reactivity and functionalism by the use of shaped laser pulses. Since the middle 1980s, the advances in the realm of nuclear dynamics driven by femtosecond laser pulses underling the theoretical proposals for different optical control schemes that rested on the dynamic response of a molecular target to the temporal shape, phase and intensity of a laser pulse. Early considerations of optical control based on the coherence properties of infrared (IR) laser radiation were advanced by Paramonov and Savva [46] and subsequently by Joseph and Manz [47]. General control concepts and schemes [5, 48, 49] rest on the Tannor-Rice theory of pump-dump control [48–50], the Shapiro-Brumer theory of coherent control [51–53], and the theory of Rabitz and his colleagues for control by the use of tailored laser fields produced by pulse shaping [54–57]. The foundations of optimal control theory by pulse shaping [5] were laid by Tannor and Rice [48] on the basis of a variational formulation, where the optimized pulses are obtained from the (radiation field dependent) functional $J = \langle \Psi(t)|\hat{P}|\Psi(t)\rangle$, where $\hat{P}$ is the projection operator selecting the desired target. The general concept was extended by Rabitz and his colleagues [54] from the perturbative domain of weak laser fields to arbitrarily strong optimal laser pulses. Another important progress was achieved by Judson and Rabitz [56] with the adaptation of algorithms for closed loop learning for pulse shaping. In the realm of control of nuclear dynamics, these significant developments were quite unique, as theory preceded experiment. These theoretical schemes stimulated significant control experiments. These were first carried out on a variety of systems with increasing size from metallic dimers and trimers to clusters [58–80], and later on complex systems of large molecules even in solution [81–93], confirming theoretically proposed concepts. This book describes progress in this important field in both experiment and theory, and strives toward the creation of a conceptual framework and experimental methodology of optical control.

To strike the last cord in this historical overview, we focus on most recent developments in the area of dynamics and control, which pertain to 'pure' electron dynamics in chemical and physical systems [94–97]. Electron dynamics involves changes in electronic states, with the nuclear motion being frozen. Characteristic temporal limits of ~ 24 attoseconds for electron dynamics, correspond to one atomic unit of time. Ultrafast dynamics and its control are currently moving from 'femtosecond chemistry' with the time-resolution of nuclear motion toward 'attosecond chemistry' with the temporal resolution of electronic motion.

The Sfb 450 research program

During the last decade the research area of ultrafast, femtosecond dynamics on the time scale of nuclear motion moved from the realm of analysis of ultrafast processes toward the new horizons of analysis and control of nuclear dynamics. These directions were advanced by the research groups participating in the Collaborative Research Center "Analysis and control of ultrafast photoinduced reactions" (Sfb 450) research program supported by the Deutsche Forschungsgemeinschaft. The central goals of the Sfb 450 program pertain to the following three interconnected elements: (i) To couple suitably designed laser fields with the electronic and nuclear level structure in a variety of molecular, cluster, surface, condensed-phase and biological systems, from small molecules with a few number of degrees of freedom to large systems with increasing complexity. (ii) To characterize the resulting nuclear-electronic motion of the system by the real-time interrogation of its dynamics. (iii) To direct the nuclear motion for the attainment of a stable product state that was not selectively obtained by conventional or by photochemical methods. To achieve these goals, it was imperative to develop methods of analysis for the interrogation and specification of the dynamics, together with the characterization of the temporal structure, amplitude, phase and intensity of the laser field that will allow for the control of the dynamics. Analysis and control of electron-nuclear dynamics driven by suitably shaped laser fields constitutes the two cornerstones of this research program. Such controlled nuclear dynamic processes in a nuclear-electronic level structure, coupled to a suitably shaped laser field, supplements and complements photoselective chemistry with additional elements of manipulation of functionality.

The first stage of this research program (1998-2001) focused on the analysis of ultrafast reactions in suitable model systems. The experimental pump-probe methodology involved excitation by an ultrashort transform-limited laser pulse, followed by the interrogation by a second, time-delayed laser pulse. The systems studied ranged from diatomics and triatomics to small metal clusters, with a small number of degrees of freedom, to complex systems, i.e., polyatomic molecules, biomolecules and large clusters in the gas phase, in liquids, in solids and on surfaces. The dynamics of the system was then reflected

in the time dependence of the signal. The experimental and theoretical work focused on dynamics in the time domain. At that early stage, the control of dynamics [46–57] was still a vision, being in the initial developmental steps from 'theoreticians' dreams' toward experimental reality. During the second period of this research program (2001-2004) control of dynamics based on the Tannor-Rice and the Rabitz schemes was experimentally realized for small systems. Suitable modulators were used in conjunction with closed-loop genetic algorithms for the shaping of the laser fields, while the theory of optimal control was applied and extended. The close interrelationship, strong interactions and complementarity between experiment and theory were instrumental for progress in this exciting research field. The complex laser fields for the attainment of optimal control, which were generated by the closed-loop learning algorithms, provided spectral components with a temporal distribution and frequency (coherently superimposed) distribution that can be mapped on the dynamics of the nuclei. These experimental and theoretical interrelationships established a novel and significant link between the two central objectives of this research program, pertaining to analysis by control. The third period of this research program (2004-2007) relies on the experimental capabilities for the generation of shaped, complex laser fields together with the theoretical concepts for the exploration of analysis and control of dynamics in complex systems, establishing the relations between controlled dynamics, reactivity and function. The chromophores were spatially and structurally enlarged, with increasing the number of active intramolecular degrees of freedom, while the number of the intermolecular degrees of freedom (of the 'bath') was increased by microscopic solvation of chromophores and by the increase of the number of ligands surrounding them. The methods for the control of dynamics, reactivity and function were extended with increasing the spectral range of the lasers from the IR to the UV spectral range over a wide intensity domain, and with the combination with static strong electric fields. The 'bottom-up' experimental and theoretical approaches adopted in this research program make significant contributions toward the establishment of an integrated approach for the understanding and operations of control of nuclear dynamics in systems of increasing complexity. The scientific information underlines the development of exquisite experimental probes and theoretical methods for nuclei 'in motion' in the course of dynamics and its control. This research will open avenues toward the future exploration of novel processes and their applications. Fundamental problems pertain to the optical control of dynamics of complex systems, to the exploration of dynamics and control in finite ultracold systems (quantum clusters and gases), as well as to the extension in the realm of dynamics and control toward 'pure' electron dynamics, with the nuclear motion being frozen. Some notable applications, which rest on basic experimental and theoretical research, involve the optical interrogation and manipulation of biological systems, as well as to the development of sensing methods in remote environments, and to the advent of optically driven molecular memory devices for quantum computing.

Perspectives

Experimental horizons

Future developments in ultrafast dynamics and its control will continue to emerge from concurrent experimental and theoretical efforts, some of which will be based on the broad scope of techniques, concepts, theories and simulations advanced in the present volume. Progress in the establishment of the conceptual framework for the field will drive toward new scientific-technological developments.

On the experimental front, the current availability of Ti:sapphire lasers, with chirped pulse and amplification methods, provide pulses (wavelengths 700-1000nm, repetition rates 50-100MHz), with pulse lengths in the range of 100fs-5fs. The shaping of fs pulses is traditionally conducted by liquid crystal modulators, with feedback control being driven by the use of genetic algorithms. The attainable temporal pulse width of 10fs is sufficient for the interrogation of ultrafast dynamics in molecules, clusters, nanostructures, condensed phase, biomolecules and biological systems on the time scale of nuclear motion. New techniques are currently advanced to transcend the fs time domain with the production of attosecond pulses [95–100], which will be of central importance for the interrogation of dynamics with the temporal resolution of electronic motion, e.g., inner-shell Auger processes in atoms and molecules, and some other processes of electron dynamics [98–100]. One central possibility for control of these 'pure' electronic processes will be achieved by changing the phase of a single laser cycle [101–104]. For dynamics with the temporal resolution of nuclear motion, the extension of the wavelength domain of fs lasers will be of considerable interest. Subfemtosecond X-ray pulses were generated [99, 105] and utilized for the interrogation of ultrafast structural dynamics, which will be alluded to below. UV and XUV ultrashort pulses by high-harmonic generation from the output of high-power near-IR lasers [94, 106] and from free-electron lasers [107] are pertinent for the interrogation of dynamics and control of electronic excitations and of ionization in solids, liquids, clusters and molecules, e.g., large gap insulators such as rare gases [108] and in highly excited molecular states. The production of ultrashort IR pulses from free-electron lasers will be significant for the intramolecular vibrational excitations and for the control of IR-induced conformational isomerization in molecules and biomolecules. The development of intense far-IR lasers in the terahertz regime is in the planning stage and will be useful for the interrogation of low-frequency intermolecular vibrational motion in large molecular scale systems and in biomolecules.

Some of the most important novel experimental developments in chemistry, physics and biology pertain to structural dynamics that involves the interrogation of time-resolved structures. The utilization of synchrotron radiation and X-ray pulses explored time-resolved dynamics on the ns-ps time scale [109–121]. This time domain is relevant for condensed phase and biological

structural dynamics. The most significant advancement and development of ultrafast femtosecond time-resolved electron diffraction, crystallography and microscopy [122–124] led to joint atomic-scale spatial and temporal resolutions [124]. Prime examples involved structural changes in 'isolated' molecules in beams, interfaces, surfaces, two-dimensional layers, nanostructures and self-assembled systems and nano-to-micro structures in materials and biological systems [124]. Time-resolved structural interrogation opens avenues for the exploration of complex transient structures and assemblies in material science, nanoscience and biology [124]. Time-resolved ultrafast X-ray diffraction methods [105, 117–120] show great promise in molecular and material science. Ultrafast X-ray pulses are currently produced from laser plasma generation (pulse widths 100-500fs). Prime phenomena that were already explored involve dynamics of melting and of phonon coherence effects.

Table-top ultraintense ultrafast lasers in the near-IR are characterized by a maximal intensity of 10^{20}-10^{22} Wcm^{-2}, which constitutes the currently available highest light intensity on earth [125–128]. Concepts were introduced for the attainment of pulses with a peak intensity as high as 10^{29} Wcm^{-2} [127, 128]. The ultraintense lasers that are currently operated in the near-IR domain span the intensity range of 10^{14}-10^{21} Wcm^{-2}, with a pulse duration of 10-100fs. Intense VUV free-electron lasers with pulse lengths of 100fs became recently operative in the intensity domain of 10^{13}-10^{14} Wcm^{-2} [107, 108]. The coupling of macroscopic dense matter with ultraintense laser fields is blurred by the effects of inhomogeneous dense plasma formations, isochoric heating, beam self-focusing and radiative continuum production [129]. To circumvent the debris problem from macroscopic solid targets, it is imperative to explore efficient laser energy acquisition and disposal in clusters, which constitute large, finite systems, with a density comparable to that of the solid or liquid condensed phase and with a size that is considerably smaller than the laser wavelength. The physics of the response to near-IR and VUV ultraintense lasers is distinct, as in the former case a quasistatic description of the laser field is applicable, while the latter case marks the failure of the quasistatic approximation for the field, as implied by the large value of the Keldysh parameter [130, 131].

The traditional control methods of fs pulses from Ti:sapphire lasers are based on the shaping of the pulse train, amplitude and phase. A significant extension of this technique to include the (linear and circular) polarization shaping of the pulse was already accomplished [132, 133], which results in 'fully shaped' near-IR pulses. Some interesting proposals for the use of linearly polarized fs pulses involve selective electron transfer [134], while circularly polarized IR π laser pulses can induce nuclear torsional motion for the preparation of pure enantiomers from an oriented racemate [135]. Regarding control in different spectral domains outside the near-IR, the newly available VUV, UV and IR ultrafast pulses cannot be shaped by the conventional devices that use liquid crystals, and new techniques will be necessary. Shaping of XUV pulses is under way [136] by phase-only shaping of the fundamental

near-IR, 800nm driver pulses for high-harmonic generation. Also, the use of conventional shaping devices for the tailoring of intense near-IR laser pulses is limited to the intensity range below $\sim 5 \cdot 10^{14}$ Wcm^{-2} due to damage to the shapers [137,138]. The control of reaction products in ultraintense laser fields (peak intensities $\geqslant 10^{15}$ Wcm^{-2}) is technically and conceptually different from the exploration of control in ordinary fields. Ultraintense field control can be achieved by using different laser parameters, i.e., pulse intensity, temporal length, shape, phase and train, in different experiments. As pulse shaping via learning algorithms is inapplicable under these experimental conditions, the changing of the laser parameters is called for. Simulation methods recently developed for multielectron ionization and electron dynamics of clusters in ultraintense laser fields [130,131] will provide guides for the experimental choice of laser pulses for optimal control. Two scenarios were recently advanced for control in ultraintense laser fields, i.e., the control of extreme multielectron ionization levels in elemental and molecular clusters [137–139], and the control of the branching ratios in nucleosynthesis driven by Coulomb explosion of completely ionized large clusters (nanodroplets) of methane, ammonia, and water [140].

Conceptual framework

In what follows we shall allude to analysis and control of dynamics of systems of increasing complexity from manipulation of functionality of clusters toward biosystems, and then address some basic open questions in the realm of control. Next, we proceed to the new world of response of clusters and plasmas to ultraintense laser fields, where nonperturbative effects are fundamental and new phenomena of multielectron ionization and electron dynamics are exhibited. These issues will bring us to progress in attosecond electron dynamics. We will conclude this presentation with the dynamics and control of matter under extreme conditions in finite, ultracold systems that involve superfluid boson, e.g., $(^4He)_n$ and $(p-H_2)_n$ clusters (temperature 2.2-0.1K) [30,141], and optical molasses (temperatures $10\mu K$-$100\mu K$) [31,141], together with the perspectives for the production of molecular and cluster species for Bose-Einstein condensation in the temperature range of $10\mu K$-$10nK$ [141–144].

The exploration of the control of ultrafast processes driven by tailored laser pulses allowed for the determination of how the optical properties, response and reactivity will be determined by the interplay between spatial structure, size (in the case of finite clusters and nanostructures systems), the system's energy landscapes, its electronic and vibrational level structure, and the nature of the laser field. Laser-selective chemistry is combined with the functionality, which is size-selective with manifestations of specific effects in finite systems. The extension of the concepts and techniques of analysis control to systems of increasing complexity, from large clusters, to large-scale chemical systems and to biological systems, will be of considerable importance and significance. It is often common to refer to the increase of the system size as

a benchmark for increasing their complexity, without alluding to more rigorous specifications. Complexity can be characterized by spatial, energetic or temporal structure with nonperiodic variations [145]. On the basis of such a definition, the control of dynamics pertains to the manipulation of complexity. An example that comes to mind is the 'transition' between fission and Coulomb explosion of multicharged, large finite systems that can be induced by laser control of the ionization level of a large molecule, of a covalent cluster [35] or of a protein in the gas phase [146]. Theoretical studies of optimal control of nuclear dynamics in complex systems in the gas phase were recently pursued [43, 147] by the Rice-Tannor-Kosloff pump-dump scheme, searching for the connective pathway between the initial wave packet and the objective. The methodology was based on molecular dynamics in conjunction with quantum computations for the transient structures across the pathway ('on the fly') [43, 147]. The maximization of the yield resulted in coupled equations for the optimal pump and dump pulses that cannot be solved for complex systems. A new strategy for pump-dump control was based on the concept of the intermediate target that involves a localized wave packet in the excited potential surface at an optimal time delay which guarantees maximal overlap for damping into the ground state objective [43, 148]. This extra condition allowed for the decoupling of the equations for the pump and the dump pulses, was tested for the isomerization of moderately large Na_3F_2 clusters, and shows promise for larger complex systems [43, 147, 148]. Another promising approach for large systems is IR control of configurational changes. Theoretical studies of the IR control of isomerization of glycine (with 24 vibrational degrees of freedom) were conducted, being based on the propagation of the ensemble of trajectories obtained from quantum chemistry computations coupled to IR fields whose parameters were optimized by genetic algorithms [149]. This approach will be relevant for conformational dynamics in building blocks for biomolecules. Two major obstacles in the development of control methods for complex large systems should be addressed. First, for large molecular scale systems and biosystems, vibrational sequence congestion implies that laser excitation carries the congested thermal vibrational population of the ground electronic-vibrational state to the excited state, blurring the excited state wave packet. In the early stages of laser photoselective chemistry [150] this difficulty was overcome by supersonic beam cooling of large molecules and of building blocks for biomolecules. Second, of considerable interest will be the control of dynamics in such complex systems in the condensed phase, e.g., in water. The implications of energetic inhomogeneous spectral shifts induced by the solvent, together with the role of the solvent as a 'heat bath' for relaxation and dephasing, require close scrutiny in the context of control.

Current progress in the realm of optimal control points toward further extensions of the conceptual framework. Under favorable conditions it should be possible to infer on the intramolecular or intracluster nuclear dynamics from the shape of the optimized pulses. This inversion problem [151, 152] constitutes the 'holy grail' that will allow for analysis by control. Since tailored

laser pulses have the ability to select pathways that optimally lead to a chosen target, the analysis of these (temporal and frequency) pulse shapes should enable to obtain information on these selected pathways. More theoretical work is required, which will allow for the design of interpretable optimal pulses for the driving of complex systems by invoking concepts for the solution of the inversion problem.

The area of laser-matter interactions is currently transcended by moving toward attosecond-femtosecond electron and nuclear dynamics in ultraintense laser fields (pulse peak intensity 10^{15}-10^{20} Wcm^{-2}). Of considerable interest is cluster electron and Coulomb explosion dynamics [130, 131, 153–178]. Extreme cluster multielectron ionization in ultraintense laser fields is distinct from electron dynamic response in ordinary fields, where perturbative quantum electrodynamics is applicable, and from the response of a single atomic and molecular species in terms of mechanisms, the ionization level and the time scales for electron and nuclear dynamics. Extreme multielectron cluster ionization involves three sequential-parallel processes of inner ionization, of nanoplasma formation and response, and of outer ionization [130, 131, 155, 158–160, 166, 172]. Cluster electron dynamics triggers nuclear dynamics, with the outer ionization being accompanied by Coulomb explosion [131, 155, 161, 164, 165, 167–169, 171, 173–178], which produced high-energy (1keV-30MeV) ions and nuclei in the energy domain of nuclear physics. A realistic endeavor pertains to table-top dd nuclear fusion driven by Coulomb explosion (NFDCE) of deuterium containing clusters [163–165, 167, 168, 173–178], for which compelling experimental and theoretical evidence was advanced. Predictions [164, 165] that Coulomb explosion of deuterium containing heteroclusters (e.g., $(CD_4)_n$, $(D_2O)_n$) will result in considerably higher deuteron energies and dd fusion yields due to energy boosting effects were experimentally confirmed in Saclay [176], in the Lawrence-Livermore Laboratory [174, 175], and in the Max-Born Institute [177]. A theoretical-computational demonstration was recently provided for a seven-orders-of-magnitude enhancement in the neutron yield from NFDCE of light-heavy heteroclusters, e.g., $(DI)_n$, as compared to the yield from deuterium clusters of the same size [178]. The eighty years quest for table-top nuclear fusion driven by chemical reactions was achieved by 'cold-hot' fusion in the chemical physics laboratory, opening avenues for experimental and technological progress. The realm of nuclear reactions driven by cluster Coulomb explosion was extended from dd fusion to nucleosynthesis involving heavy nuclei, which is of interest in the context of nuclear astrophysics [140]. Further progress in this field will involve the experimental and theoretical studies of multielectron ionization and Coulomb explosion of nanodroplets [140, 177]. Under cluster vertical ionization conditions the energetics of the nuclei is considerably enhanced (in the energy range of 100keV-100MeV) for Coulomb exploding nanodroplets. The constraints for complete inner ionization of nanodroplets have to be established. Concurrently, incomplete outer ionization and laser attenuation effects in these large systems will limit the energetic domain for the Coulomb explosion of the

bare nuclei. Interesting conceptual and technical developments are expected to emerge when cluster dynamics is transcended toward nuclear reactions.

We alluded to ultrafast adiabatic and nonadiabatic nuclear dynamics and control. Have we reached the temporal borders of the fundamental processes in chemistry and biology [179]? Indeed, the time scales for nuclear motion provide the relevant temporal limit for biophysical and biological dynamics. On the other hand, and most significantly for chemical transformations and for the response and function of nanostructures, even shorter time scales - from attoseconds to femtoseconds - can be unveiled for electron dynamics [94–97]. 'Pure' electron dynamics pertains to changes in the electronic states, without the involvement of nuclear motion, bypassing the constraints imposed by the Franck-Condon principle. In this new world, electron dynamics may prevail on the attosecond temporal resolution. An interesting development in the area of attosecond-femtosecond electron dynamics constitutes a 'spin off' of ultraintense laser-cluster interactions (discussed above) which drive phenomena of nanoplasma response and dynamics. Two notable and related developments in the realm of electron dynamics in intense fs laser fields recently emerged. First, the advent of nonsequential double ionization, involving (e,2e) recollision processes [94,180–185], provides significant information (from the electron momentum correlation function) on the electronic wavefunction of the target molecule from which the electron departed [184]. From the practical point of view, the electron can diffract from the molecular ion core, determining the spatial structure of the molecule [180,186]. The (e,2e) processes in atoms result in nonsequential ionization from the same core, while for molecules or clusters these processes can occur from different cores. Work on (e,2e) processes in diatomics [184] and in the C_{60} molecule [180] was already conducted. It will be interesting to extend these aspects of (e,2e) dynamics to elemental and molecular clusters. Second, single- (or sub-) optical cycle lasers driving atoms provides novel dynamic information on cycle and phase dependent electric field induced ionization rates and electron recollision times [101–104]. Coherent control experiments of electron dynamics demonstrated the possibility of directing fast electron emission from Xe atoms to the right or to the left with changing the light phase [102]. Of considerable interest will be the extension of these studies of electron dynamics driven by single (or few) optical cycle lasers in molecules and in elemental and molecular clusters.

The theory of electron dynamics in small molecules, driven by attosecond laser pulses, was advanced by Bandrauk [187–189]. Recent theoretical studies and quantum mechanical calculations [190, 191] addressed optimal ultrafast (6fs) lasers driving electron dynamics in molecules, establishing the scheme for state selective electronic excitation involving dipole switching in lithium cyanide [190] and the formation of a 'giant dipole' in N-methyl-6-quinolone [191]. A new mechanism was advanced for the induction of a selective, unidirectional electron ring current in oriented molecules driven by electronic excitation with a circularly polarized ultrashort (3.5fs) laser pulse [192, 193]. The implications of this proposal were examined for $X \rightarrow E_+$ population

transfer, described by electron wave packet dynamics, in Mg-porphyrine. The ring current generated by the laser pulse is stronger by about two-orders-of-magnitude than that induced in this system by the available permanent magnetic field [192]. It was suggested that these types of specific electronic currents may in turn induce magnetic fields with characteristic effects on superconducting quantum interference devices [192]. These studies provide clues for the extension of electron dynamics to multielectron dynamics in large molecules.

The exploration of 'pure' electron dynamics without the involvement of nuclear motion is not limited to the attosecond-femtosecond time scale and can be realized on longer time scales, when the electron motion is slow. This is the case for the dynamics of wave packets of electronic high n Rydberg states of atoms [194–201], which circulate along classical Kepler paths with diameters of thousands of Bohr radii on the microsecond time scale. While such electronic wave packets driven by ps pulses lead to Rydberg state ionization near the turning point of the Kepler orbit, subpicosecond, half-cycle pulses can ionize a radially localized Rydberg wave packet over its entire trajectory [200]. New avenues for the exploration of 'slow' electron dynamics open up. The dynamics of Rydberg wave packets in molecules [201], e.g., NO, is also of considerable interest. For high n molecular Rydbergs the electron motion is slow on the time scale of nuclear motion, and the inverse Born-Oppenheimer separability has to be invoked. Rydberg electronic wave packets exhibit nonadiabatic coupling with other degrees of freedom, and are amenable to control by interference effects [201].

Significant developments encompass the realm of dynamics of ultracold finite systems [141], involving molecules, clusters, optical molasses and finite Bose-Einstein condensates in the temperature domain of T = 2.7K-10^{-8}K [141]. For ultracold systems, the upper temperature limit (T = 2.7K) is arbitrarily taken as the current temperature of the expanding universe, while the lowest temperature is chosen as that of low-density atomic or molecular Bose-Einstein condensates [141]. The higher temperature domain of the ultracold world for large molecules, e.g., aniline and anthracene (with rotational temperatures of 0.3K-2.7K), was reached by cooling in supersonic expansions in He from high-pressure pulsed supersonic nozzles [202], allowing for the study of kinetic energy and permutation symmetry effects in anthracene$(^4\text{He})_n$ clusters [202]. Small molecules were cooled to the mK temperature range [203–206] by deceleration and electrostatic trapping of OH radicals at (rotational) temperatures of 50-500mK [205], and of the $^{15}\text{ND}_3$ molecule at a temperature of 1mK [206]. The relatively deep and spatially large traps for ground state, neutral, ultracold molecules show promise [203–206] for high-resolution spectroscopic and dynamic applications in large molecules and clusters. Exotic ultracold systems encompasses quantum clusters $(^4\text{He})_n$, $(^3\text{He})_n$, or (para-$\text{H}_2)_n$ (at T = 0.1-2.2K) [30,141,207,208], optical molasses of irradiated Rb atoms (T = 10^{-4}-10^{-6}K) [31], finite atomic clouds of Bose-Einstein atomic condensates of ^7Li, ^{23}Na, and ^{87}Rb (T = 10^{-7}-10^{-8}K) [209–211], and finite Bose-Einstein

molecular condensates of clouds of diatomics, e.g., $^6Li_2$, $^{23}Na_2$, or $^{87}Cs_2$ (at T $= 10^{-8}$-10^{-7}K) [144–146,212–222]. Some notable example for dynamics in the ultracold world are: (i) The expansion of optical molasses, which is analogous to cluster Coulomb explosion, thus building a bridge between the ultraslow (ms) dynamics of ultracold finite gaseous samples and ultrafast (ps-fs) cluster dynamics [31]. (ii) The tunneling of an excess electron from a bubble in $(^4He)_n$ clusters, as a probe for superfluidity in finite boson systems [223]. The unique properties and features of ultracold quantum clusters, optical molasses and atomic and molecular gases, can be traced to quantum effects of zero-point energy and kinetic energy of the 'light' constituents in clusters and permutation symmetry effects in all systems. Outstanding problems in this field involve size effects on the superfluid transition in helium-4 clusters [141], energetics of excess electron bubbles in large helium clusters [223], electron tunneling dynamics from such bubbles that constitute a 'pure' electron dynamic process on the ms time scale [223], finite size effects on Bose-Einstein condensation in confined systems [141], probing superfluidity in finite boson systems, and a molecular description of Bose-Einstein condensation [141]. Interesting further developments in this field will focus on collective excitations, as well as nuclear and electron dynamics in large finite quantum systems. These will involve the attempt for the production of finite ultracold clusters. Two distinct classes of such ultracold clusters will be considered, involving either highly vibrationally excited 'floppy' clusters (produced via Feshbach resonances) [212–222] or rigid clusters in low vibrational states produced by photoassociation [144–146]. It will be interesting to explore the possibility of Bose-Einstein condensation in ultracold assemblies of such clusters. Another interesting problem pertains to the minimal cluster size for the attainment of Bose-Einstein condensation within a single cluster [141]. The threshold size for the superfluid transition in a boson cluster is expected to be property dependent [141]. Other interesting problems in this area pertain to the theoretical investigation of optically induced tunneling of electrons from bubbles in helium clusters [223]. This process can be controlled by the competition between electron tunneling from the bubble and ultrafast radiationless (nonadiabatic or adiabatic) relaxations of the bubble excited electronic states to lower electronic states. The exploration of electron tunneling from electronically excited states of electron bubbles in ultracold quantum clusters brings us back to the realm of laser control of electron dynamics.

Scientific-technological applications

The research directions and developments discussed herein provide perspectives for new scientific-technological developments. A number of research directions within the framework of the Sfb 450 program reach a stage when one can begin to consider technological spin-offs. Examples involve remote laser manipulation, analytic and sensing methods [224–226]. Recent accomplishments involve the use of half cycle laser pulses for the chemical analysis [226], and remote sensing by multiple filamentation of ultrashort Terawatt laser pulses in air [224, 225]. Optical manipulation of complex systems

shows promise for applications to biological systems. Primary examples in this field are photodynamic therapy, based on optical manipulation of molecules with endoperoxide groups [227], and the detection of biological molecules in tissues [228]. The analytical methods have potential for probing biosystems, e.g., bacteria, while sensing methods and controlled dynamics of atmospheric processes is of current interest. Although the primary thrust of the research program is based on the integration of experiment and theory, it is imperative to mention some theoretical developments of considerable interest in the context of future technology transfer. The first is molecular motors, due to their important role as functional molecular devices [229–235]. Chiral molecular rotors were described, being driven by a linearly polarized laser pulse [229, 231, 233–235], with the application of control methods for the preselected directions [231]. Unidirectional molecular torsional motion can also be induced by circularly polarized π laser pulses for the driving of such molecular rotors. Potential applications in the field of nanotechnology will be of interest. The second is optically pumped and probed logic machines for quantum computing. Elaborate molecular machines for information storage and disposal can take advantage of the self evident, but most useful, fact that the optical response of photophysical systems depends on their present state [231]. It was proposed [236, 237] that the stimulated Raman adiabatic passage spectroscopy (STIRAP) [238] can be used for information storage and retrieval on the molecular level. The utilization of the STIRAP pulse sequence provides a strategy for complete and robust population transfer in a multilevel system with sequential coupling [237, 239]. In fact, the use of the STIRAP pulse sequence for this problem emerged automatically from the local optimization procedure [239]. STIRAP spectroscopy is of considerable importance for quantum computation via local control [237], to build finite-state molecular machines that can be programmed [236, 237]. An alternative approach is based on optimal control for quantum computing [240, 241].

It is apparent that more experimental and theoretical developments are expected in this fascinating research area, some of which should emerge from this overview. It is expected that the scientific quality, vitality and impact of this research field of analysis and control of ultrafast photoinduced reactions will continue well into the future.

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