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COUPLED ELECTRON-NUCLEAR DYNAMICS
AND LIGHT PROPAGATION
IN METAL CLUSTER NANOSTRUCTURES

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ABSTRACT

In the present thesis, ultrafast relaxation processes in small noble-metal clusters are theoretically investigated in the frame of the time-dependent density-functional theory and the field-induced surface-hopping method. The interplay between electronic relaxation within a manifold of excited electronic states and nuclear rearrangement arising due to the coupling between electronic and vibrational degrees of freedom is studied in small neutral silver and anionic gold clusters. These systems have gained significant experimental attention due to their unique optical and electronic properties. It is revealed that all the studied noble-metal clusters possess long-living excited states, but the processes invoked by a laser excitation are significantly different. In the Ag_8 cluster these involve substantial nuclear rearrangement on the sub-picosecond time scale resulting in the cluster isomerization. In contrast, the Au_7^- cluster exhibits ultrafast bulk-like electronic relaxation to lower-lying excited states without noticeable changes of the nuclear configuration if the exciting pulse promotes it to the dense manifold of d-derived electronic states. Under the same conditions, the electronic relaxation in the Au_3^- cluster occurs on the sub-nanosecond time scale, and the nuclear vibrational motion eventually leads to cluster fragmentation in the excited state. Since in most chemical applications the clusters are dissolved in a liquid, the effects of solvent molecules on the relaxation processes are studied in this thesis as well.

Aiming to propose a new ultrafast observable for pump-probe experiments, in which the coupled electron-nuclear dynamics is interrogated, a method to simulate time-resolved high-harmonic spectra of photoexcited noble-metal clusters is developed. Employing this method, it is shown that the isomerization of the Ag_8 cluster can be clearly identified in the time-resolved high-harmonic spectrum. In general, it is demonstrated that the high-harmonic emission is highly sensitive to the instantaneous electron-nuclear configuration of a metal cluster and thus can serve as an ultrafast observable to be measured in time-resolved pump-probe experiments.

After the relaxation processes in the individual clusters have been revealed, the focus is drawn to collective properties of metal-cluster arrays, since these represent a novel interesting material with promising applications in nanotechnology. For this purpose, the theoretical methodology is developed, which allows for simulation of the absorption spectra and coupled electron dynamics induced by an external laser pulse in moderate-sized spatially-organized metal-cluster aggregates. This approach is applicable not only to metal cluster arrays with well-separated constituents, but also to arrays deposited on a support, where the distance between subunits does not exceed their size. Furthermore, an approximation to simulate the electron dynamics in large-sized arrays is introduced.

By coupling the developed methodology to the classical electrodynamics, the spatio-temporal distribution of the electric field can be calculated, which grants a theoretical technique to investigate the light propagation and exciton transfer in metal-cluster arrays of, in principle, arbitrary size and constitution. The approach is employed to control the direction of the light propagation in a T-shaped structure built up of Ag_8 clusters and to demonstrate the chiral properties of a ring structure made of porphyrin- Ag_4 subunits. In general, the developed theoretical methodology provides a useful apparatus for design and investigation of nanosized optical devices using the noble-metal clusters as unit building blocks.

ZUSAMMENFASSUNG

In der vorliegenden Dissertation werden ultraschnelle Relaxationsprozesse in kleinen Edelmetallclustern unter Verwendung der zeitabhängigen Dichtefunktionaltheorie und der feldinduzierten Surface-Hopping-Methode theoretisch untersucht. Das Wechselspiel zwischen Relaxation innerhalb der angeregten elektronischen Zustände einerseits und Umlagerung der Kerne andererseits, das aufgrund der Kopplung zwischen elektronischen und Kern-Freiheitsgraden entsteht, wird für kleine neutrale Silbercluster und anionische Goldcluster erforscht. Diese Systeme haben starkes experimentelles Interesse geweckt, da sie einzigartige optische und elektronische Eigenschaften aufweisen. Es wird gezeigt, dass alle untersuchten Edelmetallcluster langlebige angeregte Zustände aufweisen, jedoch die Prozesse, die durch Laseranregung initiiert werden, ausgesprochen unterschiedlich sein können. So findet im Ag_8 -Cluster eine starke Umlagerung der Kernkonfiguration auf der Pikosekunden-Zeitskala statt, wodurch es zur Isomerisierung des Clusters kommt. Im Gegensatz dazu zeigt der Au_7^- -Cluster, wenn die Laseranregung in den Bereich der d-artigen elektronischen Zustände erfolgt, eine ultraschnelle elektronische Relaxation in tieferliegende angeregte Zustände, die ähnlich zum Verhalten in Festkörpern ohne wesentliche Änderungen der Kernkonfiguration abläuft. Unter den gleichen Bedingungen erfolgt die elektronische Relaxation im Au_3^- -Cluster auf der Sub-Nanosekunden-Zeitskala, wobei die Schwingungsbewegung der Kerne letztlich zur Clusterfragmentierung im angeregten Zustand führt. Da in den meisten chemischen Anwendungen die Cluster in gelöster Form vorliegen, wird im Rahmen dieser Dissertation auch der Einfluss von Lösungsmittelmolekülen auf die Relaxationsprozesse untersucht.

Mit dem Ziel, eine neue ultraschnelle Observable für die Abfrage der gekoppelten Kern-Elektronendynamik in Pump-Probe-Experimenten vorzuschlagen, wird eine Methode zur Simulation der Spektren hoher Harmonischer in optisch angeregten Edelmetallclustern entwickelt. Mithilfe dieser Methode wird nachgewiesen, dass die Isomerisierung des Ag_8^- -Clusters eindeutig in den zeitaufgelösten Spektren hoher Harmonischer identifiziert werden kann. Allgemein wird gezeigt, dass die Emission hoher Harmonischer hoch empfindlich gegenüber der instantanen Konfiguration der Elektronen und Kerne in Metallclustern ist und daher als Observable dienen kann, die in zeitaufgelösten Pump-Probe-Experimenten gemessen wird.

Nach der Aufklärung der Relaxationsprozesse isolierter Cluster wird der Blickpunkt der Arbeit auf die kollektiven Eigenschaften von Metallcluster-Aggregaten gelegt, da diese neuartige, interessante Materialien mit vielversprechenden Eigenschaften für die Nanotechnologie darstellen. Zu diesem Zweck wird die notwendige Methodologie entwickelt, welche die Simulation von Absorptionsspektren und der gekoppelten, durch einen äußeren Laserpuls initiierten Elektronendynamik in mittelgroßen Metallcluster-Aggregaten ermöglicht. Dieser Ansatz kann nicht nur auf räumlich weit getrennte Metallcluster-Aggregate angewendet werden, sondern auch auf solche Anordnungen, bei denen die Cluster auf einem Trägermaterial aufgebracht sind und der Abstand zwischen den einzelnen Untereinheiten nicht deren Ausdehnung übersteigt. Darüber hinaus wird eine Näherung zur Simulation der Elektronendynamik in sehr großen Aggregaten eingeführt.

Durch die Verbindung der so entwickelten Methodologie mit der klassischen Elektrodynamik kann die räumliche und zeitliche Verteilung des elektrischen Feldes berechnet werden. Dies gibt ein theoretisches Verfahren an die Hand, mit dem Lichtausbreitung und Exzitonentransfer im Prinzip in Metallcluster-Anordnungen beliebiger Größe und Zusammensetzung untersucht werden können. Die Methode wird eingesetzt, um die Lichtausbreitung in einer T-förmigen Struktur aus Ag_8 -Clustern zu steuern, und um die chiralen Eigenschaften einer Ringstruktur aus Porphyrin- Ag_4 -Einheiten nachzuweisen. Im Allgemeinen liefert die hier ausgearbeitete theoretische Methodologie ein nützliches Handwerkszeug für die Entwicklung und Erforschung nanoskaliger optischer Bauelemente, die aus Edelmetallclustern als Basiskomponenten aufgebaut sind.

PUBLICATIONS

THE FOLLOWING PUBLICATIONS CONSTITUTE THE MAIN PART OF THE THESIS:

1. P. G. Lisinetskaya, R. Mitrić „Simulation of laser-induced coupled electron-nuclear dynamics and time-resolved harmonic spectra in complex systems“. *Phys. Rev. A* **2011**, *83*, 033408.
2. P. G. Lisinetskaya, C. Braun, S. Proch, Y. D. Kim, G. Ganteför, R. Mitrić „Excited state nonadiabatic dynamics of bare and hydrated anionic gold clusters $\text{Au}_3^-[\text{H}_2\text{O}]_n$ ($n = 0-2$)“. *Phys. Chem. Chem. Phys.* **2016**, *18*, 6411-6419.
3. P. G. Lisinetskaya, R. Mitrić „Ab initio simulations of light propagation in silver cluster nanostructures“. *Phys. Rev. B* **2014**, *89*, 035433.
4. P. G. Lisinetskaya, R. Mitrić „Optimal control of light propagation and exciton transfer in arrays of molecular-like noble-metal clusters“. *Phys. Rev. B* **2015**, *91*, 125436.

THE FOLLOWING PUBLICATIONS ARE INCLUDED IN THE APPENDIX:

1. J. Stanzel, M. Neeb, W. Eberhardt, P. G. Lisinetskaya, J. Petersen, and R. Mitrić „Switching from molecular to bulklike dynamics in electronic relaxation of a small gold cluster“. *Phys. Rev. A* **2012**, *85*, 013201.
2. P. G. Lisinetskaya, M. I. S. Röhr, R. Mitrić „First principles simulation of light propagation and exciton dynamics in metal cluster nanostructures“. *Appl. Phys. B* **2016**, *122*, 175.

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INTRODUCTION



Figure 1.1: The Lycurgus cup [1] seen in the transmitted (left panel) and reflected (right panel) light. ©Trustees of the British Museum

Already centuries ago, the outstanding optical properties of noble metal nanoparticles have been utilized even without proper understanding of the underlying physical phenomena. One of the real masterpieces of art and technology, which came to us from ancient times, is the famous Lycurgus cup [1] shown in Fig. 1.1. The glass vessel of this cup is known for a spectacular feature: to appear green-colored in reflected and red-colored in transmitted light. Only in 1950th it was found, that the effect is mainly caused by silver-gold colloidal particles typically of 50-100 nm size with Ag/Au ratio of roughly 7/3 dispersed in the glass [2, 3] with gold being mainly responsible for the red transmission and silver for the green reflection. It is difficult to imagine that the ancient roman glass-makers were able to control the particle growth during the glass production process, and we can only conjecture the number of unsuccessful attempts preceding the creation of the masterpiece. The difference is tremendous to modern technology, which allows for controllable creation of various metal, organic or hybrid particles with the size ranging from several Ångström to hundreds of nanometers. This impressive technological progress would not be possible without thorough and intense experimental and theoretical research, the results of which it rests upon.

In the current Chapter the main experimental and theoretical findings on the relaxation dynamics and optical properties of noble-metal nanoparticles and nanoclusters are summarized. First, in Sec. 1 the focus is drawn to the conven-

tional metal nanoparticles in the size range 50-200 nm. Subsequently, Sec. II is devoted to the description of the relaxation processes and optical response of ultra-small noble metal clusters in the size regime, where “each atom counts”. The emphasis is made on the distinctions between the processes and trends in the nanoclusters as compared to the larger nanoparticles, which arise due to the intrinsic quantum nature of the former. Further, in Sec. III theoretical approaches for simulation of individual and collective optical properties of nanomaterials are reviewed and their applicability to the noble-metal clusters is discussed. The theoretical methods for simulation of the coupled electron-nuclear dynamics in complex systems are highlighted in Sec. IV. Finally, the goal and structure of the current thesis are presented in Sec. V.

I OPTICAL PROPERTIES OF METAL NANOPARTICLES

I.1 *Plasmon resonances*

One of the first experimental investigations of light interaction with ultra-small metal objects is attributed to Faraday [4], who described in 1857 the change in color of the light transmitted and reflected by thin metallic films of sub-wavelength thickness and by metal particles of sub-wavelength size with emphasis on the influence of size and material of the particles on the color of the light beam. Nowadays the physical background of the striking colors of the small noble-metal particle dispersions is well understood. The reason is, that metal nanoparticles possess a relatively narrow absorption band in the visible region of the spectrum, which is absent in bulk counterparts as well as in individual atoms. This band is known as the plasmon absorption band or the plasmon resonance, and is attributed to collective oscillations of conductive electrons in a metal particle [5]. Numerous theoretical and experimental investigations have proven that the position and shape of the plasmonic absorption band strongly depend on the shape, size and material of a nanoparticle as well as on the surrounding dielectric environment [6–11]. In particular, it has been demonstrated both experimentally and theoretically, that the maximum of the absorption spectrum of noble-metal nanoparticles is shifted towards lower energies with increase of the particle size [12–17], if the shape of the particle is not changed. This is also valid for core-shell nanoparticles, if the shell thickness is preserved [8]. Additionally, the substantial broadening of the absorption peak with increase of the nanosphere diameter has been reported [18]. With the shape of a particle changed gradually from a sphere to an oblate spheroid of the same volume, the absorption band corresponding to dipolar excitation is monotonously broadened and red-shifted [19], while the quadrupolar contribution vanishes. The shape transformation from a spherical to a prolate spheroidal or to a nanorod also results in red-shift of the plasmon absorption

band [10, 15, 20]. Further adjustment of the position and width of the plasmonic absorption band can be realized by changing the dielectric properties of a surrounding medium [7, 15, 21] or by altering the separation to a metallic substrate or another neighboring particle [13, 19, 22, 23].

The wealth of experimental and theoretical results proves, that the optical properties of the nanoparticles with characteristic sizes above 10-20 nm do not only scale with the particle's size and shape, but also with its composition. For example, a gold-silver nanoparticle with gradually increasing concentration of silver exhibits a monotonous shift of the plasmonic absorption band from the values corresponding to a pure gold particle to that of a pure silver one [24]. Therefore, by adjusting the above described parameters, in principle, it is possible to design a system which operates at any desired wavelength in the visible, near-infrared or near-ultraviolet parts of the spectrum. In practice, recently developed lithographic and chemical methods allow for fabrication of nanoparticles with well-defined sizes and complicated shapes [10, 12, 20, 25–27]. Moreover, modern technology provides creation of nanoparticle assemblies with particular spatial organization [28].

Naturally these novel materials attract attention not only from the fundamental point of view, but also inspire an intense search for applications in science and technology. For example, the strong non-uniform electric field near a nanoparticle's surface or between several nanoparticles [29–31] can be used to enhance the optical signal from a molecule [10, 16, 32], which is interesting for analytical and bioanalytical applications such as sub-wavelength imaging, biosensing and single-molecule detection [20, 33]. Since the absorption peak maximum is strongly dependent on the dielectric environment, it can be utilized for sensing purposes [7]. Furthermore, the noble-metal nanoparticles find their applications in medicine for drug delivery [20, 33] and photo-thermal therapy [10].

1.2 *Relaxation dynamics*

The relaxation dynamics occurring in the conventional noble-metal nanoparticles upon laser pulse excitation typically involves the electron-electron (e-e), electron-phonon (e-ph), and phonon-phonon (ph-ph) scattering processes [34]. The e-e scattering leads to thermalization of initially excited electrons by internal energy redistribution within the electron gas, parallel to it a part of energy is transferred to the ionic lattice of the nanoparticle via e-ph interaction, and finally the excess of energy absorbed by the nanoparticle decays due to phonon coupling of the nanoparticle to a surrounding medium. The time constants of e-e and e-ph processes lie in the sub-picosecond to picosecond range and scale with the nanoparticle size in the size range below ~ 20 nm (this threshold size is related to the mean free path of electrons in bulk material and thus depends

on the composition of the particle). For larger nanoparticles, they become almost identical to the bulk values [35, 36]. The characteristic times for ph-ph interaction are typically around hundreds of picoseconds [34].

Notably, the decrease of the e-e and e-ph thermalization time constants for nanoparticles with sizes below ~ 20 nm leads to broadening of the plasmon absorption band [37]. Regarding the fact, that for larger particles the radiative damping results in the line broadening as well [18], it is suggested, that the plasmon absorption band has a minimal width for noble-metal nanoparticles in this size region [38, 39].

Another interesting property of the relaxation dynamics in the metal nanoparticles is the pronounced linear increase of the e-ph decay time with the increase of the power of the exciting laser pulse [36, 40]. This effect is attributed within the electronic gas approach to the linear dependence between the e-ph relaxation time and the electronic gas temperature. Higher laser intensity results in higher temperatures of the electron gas, thus increasing the relaxation times.

In summary, the relaxation dynamics in noble-metal nanoparticles plays a minor role in the optical response of the particles with characteristic sizes above ~ 20 nm. For smaller particles the effect is noticeable, but consists mainly in a broadening of the plasmonic absorption band. In contrast, further reduction of size towards the sub-nanometer clusters leads to the regime, where “each atom counts” and thus the relaxation dynamics has dramatic impact on the optical response of nanoclusters [41]. This effect is discussed in detail below in Sec. IV.

1.3 Plasmon propagation

The coupling between two and more nanoparticles results not only in changes of the position and width of the plasmonic absorption band. In addition, it can cause collective properties of such an aggregate which are absent in individual constituents, for example, chirality [42]. Furthermore, it can lead to energy transfer between the nanoparticles [43, 44], which can be interpreted as the plasmon propagation. Ultimately, using the nanoparticles as unit building blocks, ultra-small energy transmission lines [45, 46] can be constructed, leading eventually to a tremendous miniaturization of optical and electronic devices.

Of particular interest is the possibility to control the electromagnetic energy distribution in space and time within such noble-metal nanocluster aggregates. It has been theoretically predicted, that the spatial localization of the excitation energy on a femtosecond time scale in aggregates constructed of nanoscale subunits can be achieved by a phase-modulated ultrashort pulse [47, 48]. The effect underlying the coherent control procedure is the plasmon localization in inhomogeneous structures depending on the frequency of the exciting pulse [49, 50].

Since the phase modulation leads to a complicated electromagnetic pulse containing components with different frequencies interacting with the sample at slightly different instants of time, the possibility to control the plasmon localization site was expected and successfully simulated. Subsequent theoretical studies demonstrated the possibility to optimally control the spatio-temporal electric near-field distribution in nanostructures [51] and the plasmon propagation in T-shaped structures consisting of 50 nm sized silver nanospheres [52–54] using amplitude, phase and polarization modulated optical pulses. Parallel to the theoretical developments, intensive experimental investigations were performed. Impressive results were achieved by Aeschlimann *et al.* [55], who demonstrated ultrafast localization of the electric near-field in a Y-shaped array of 180 nm-sized silver disks on a sub-wavelength scale by applying a polarization-shaped femtosecond laser pulse. Subsequently, the possibility to control the near field distribution not only spatially, but also in time was proven [56]. These aspects of the light-matter interaction attract a great deal of attention not only from the fundamental point of view, but can also find their application in designing of novel plasmonic switches [57] and nanoscale sensors [58], in sub-wavelength imaging [59] and high-resolved spectroscopy [51, 60].

II OPTICAL RESPONSE OF MOLECULAR-LIKE NOBLE-METAL CLUSTERS

II.1 *Optical properties*

Further reduction of size of a single plasmonic particle leads eventually to the size-regime where “a nanoparticle meets a molecule”. Here the term “nanoparticle” is no longer conventionally used and one speaks about a “cluster” or a “molecule”. These nanoclusters consist of up to several tens or hundreds of atoms and naturally, the exact number of atoms and their mutual configuration start to play a decisive role in determining the optical response of a cluster. In this size regime where “each atom counts” the absorption bands characteristic for the plasmon resonances of the conventional nanoparticles are transformed to a number of individual absorption peaks corresponding to the geometric structure of the cluster [61–63], which is a fundamental difference between the small clusters and the large plasmonic nanoparticles. Therefore, establishing of some general laws governing the absorption peak location and bandwidth, similar to those for conventional nanoparticles discussed in Sec. 1.1, does not seem possible in the case of ultra-small metal clusters [64]. The similarities or trends sometimes observed in absorption or photoelectron spectra [65] should be considered as coincidences rather than rules.

Thorough studies of ultra-small noble metal clusters in the recent decades have provided a wealth of information on their optical properties. It has been experimentally demonstrated, that these particles exhibit fluorescence with par-

ticularly high quantum yield [66–69], which can be tuned by adjusting the cluster size and solvent to cover the whole visible spectral region [70]. Due to good biocompatibility, the fluorescent properties of metal nanoclusters can be employed in optical labeling and bio-imaging [71]. Moreover, noble-metal clusters possess higher two-photon absorption cross-sections as compared to many organic chromophores [72, 73], which is essential for biological imaging and sensing applications. Lower photon energies used to excite fluorescence result in lower scattering and autofluorescence, which increases the penetration depth and spatial resolution [74]. As a result of the interaction of noble-metal clusters with some metal ions or biomolecules, the fluorescence signal is quenched, providing an efficient instrument for detection of these particular species [75–78]. On the other hand, in various metal cluster-biomolecule hybrid systems the inherent weak absorption or fluorescence of a biomolecule can be significantly enhanced [79, 80].

II.2 *Relaxation processes*

Numerous theoretical and experimental studies have demonstrated, that the optical response of noble-metal clusters is altered in a non-scalable manner not only with changing the number of atoms even by one, but also with nuclear arrangement [81–86]. This leads to the second important difference between metal clusters and conventional nanoparticles, namely, the significant influence of the photoinduced nuclear dynamics on the optical response of the cluster. While for nanoparticles this effect does not play an essential role due to the large number of atoms in the structure, in sub-nanosized metal clusters the ultrafast dynamical processes occurring under an external electric field excitation become of extreme importance, because they can dramatically change the optical properties of a cluster on a femtosecond time scale [41, 87–89]. This is one of the reasons why the investigation of the ultrafast coupled electron-nuclear dynamics attracts much attention these days both from the experimental and theoretical point of view [90–96].

Besides the non-radiative electronic relaxation and energy redistribution between nuclear and electronic degrees of freedom, which can be considered as analogues to e-e and e-ph scattering in conventional nanoparticles, the relaxation processes in metal nanoclusters often involve significant nuclear rearrangement leading to changes in chemical bonds, isomerization, or even fragmentation of the metal cluster already at low intensities of the excitation field [97–99]. As well as the absorption spectra, the characteristic time constants of relaxation processes in ultra-small noble metal clusters do not scale with the cluster size [100]. Moreover, even the processes induced can differ, if the atomic composition, charge, geometry configuration, environment or energies of exciting laser photons are changed [101–106]. Therefore, each particular clus-

ter exposed to various external conditions requires independent theoretical and experimental investigation.

In general the coupled electron-nuclear dynamics and relaxation processes occurring in noble-metal clusters remain by now largely unexplored. The attention is focused mainly to several species with well-established production technology, which are proven to have novel chemical or optical applications. One of the brightest examples is the spherical ligand-protected Au_{25} cluster. It can be produced with molecular purity [107], which is important for accurate experiments, and consists of an icosahedral Au_{13} core surrounded by an Au_{12} -ligand shell. The precise manufacturing technology allowed for performing of an X-ray crystallographic analysis to interrogate this unusual cluster structure [85] and to study the relaxation processes in this cluster employing transient absorption measurements [103]. In the same manner, the rod-shaped ligand-protected Au_{25} cluster was investigated [104]. The relaxation dynamics in the rod-shaped cluster involved non-radiative electronic decay to the lowest excited electronic state within ~ 0.8 ps and subsequent slow relaxation to the ground state with a time constant of $2.4 \mu\text{s}$. In contrast, the relaxation processes observed in the spherical Au_{25} cluster involve electronic relaxation of the Au_{13} core as well as core-shell energy conversion [103, 108]. The discussed example demonstrates, that even for such an interesting and well-studied cluster as Au_{25} , the relaxation processes are largely dependent on the precise structure, and a proper interpretation of the experimental findings requires thorough theoretical study.

Another group of metal clusters, the relaxation processes in which have been recently experimentally studied, are small noble-metal anionic clusters consisting of up to 20 atoms [92, 100–102, 109, 110]. These clusters are produced by the laser vaporization technique [111] and mass-selected afterwards, which allows for precise selection of the atomic composition. The relaxation dynamics has been investigated by means of time-resolved photoelectron spectroscopy. For small silver anions, excited state lifetimes of hundreds of femtoseconds were determined, despite the “magic” Ag_7^- cluster, which possesses long-lived excited states with decay times of several picoseconds. The studied small anionic gold clusters demonstrated the strong dependence of the relaxation dynamics on the cluster size. Strikingly, an extremely long excited state lifetime of the Au_6^- cluster is observed, which exceeds 90 ns. Concurrent theoretical studies gave a clear explanation of the ultrafast relaxation processes in gold clusters of different size, namely, electron-nuclear coupling inducing vibrational motion in Au_5^- clusters and fast internal conversion with subsequent cluster melting in Au_7^- and Au_8^- .

The provided examples demonstrate, that the relaxation processes and their time scales vary dramatically for small noble-metal clusters and accurate theoretical investigations are strongly required to interpret the experimental results.

II.3 *Exciton transfer in molecular-sized cluster assemblies*

As it was mentioned in Sec. 1.3, the strong coupling between closely placed metal nanoparticles leads to energy transfer between them and opens a striking possibility to control the spatial and temporal electric field distribution as well as the energy propagation in nanoparticle aggregates. In a structure built up of ultrasmall noble-metal clusters the role of a plasmon can be performed by an exciton. The questions arise, whether exciton transfer can effectively occur in metal nanocluster aggregates and if it can be controlled in the same manner as in the conventional nanoparticles. Unfortunately, up to now no experimental evidence of such effects is reported, and thus theoretical simulations are required to answer this question. As compared to the optical and dynamical properties of noble-metal nanoclusters discussed above, the issue of energy transfer and exciton propagation in ultra-small metal-cluster arrays has attracted much less attention by the scientific community these days, probably due to the complexity of the experimental realization. On the other hand, the experimental techniques for the fabrication of metal structures develop rapidly [70, 112–114] and one can be hopeful, that in some years the frontiers of cluster nanoscience will cover the manufacturing of nanocluster arrays and observation of energy transport within them.

III THEORETICAL DESCRIPTION OF THE OPTICAL RESPONSE IN NANOCCLUSERS

III.1 *Classical electrodynamics*

After Maxwell had presented his famous set of equations [115] establishing definite relations between the electric and magnetic field vectors and macroscopic material properties, the researchers obtained a powerful instrument for rigorous study and explanation of the phenomena related to electromagnetic field propagation and interaction with matter. Within the classical Maxwell approach each medium or object is characterized by dielectric and magnetic material functions. In general, the particles interacting with light in the classical electrodynamics are considered as partially-continuous media or ultimately point objects with dielectric properties determined either based on the properties of the bulk counterparts, in some cases including shape and size corrections [116, 117], or measured in additional experiments.

SINGLE-PARTICLE METHODS A vast variety of methods has been developed to simulate the optical response of the conventional nanoparticles with sizes, although smaller than the wavelength of an incident electromagnetic field, but still large enough for a bulk-like description to be valid. The numerical ap-

proaches, which require the discretization of the nanoparticle surface, like the boundary element method (BEM) [118], or of the whole simulation domain, like the finite-difference time-domain (FDTD) [119] and the finite-element (FEM) [120, 121] methods, can not be straightforwardly applied to nanoclusters. This is due to the vagueness in defining the border between a nanocluster and a surrounding medium, especially when clusters consisting of up to few tens of atoms are considered.

The Mie solution [122, 123], which was derived for a spherical particle of arbitrary size, can be in principle employed to determine scattering and absorption spectra of a very small particle with uncertain borders, provided an effective radius is given and proper size corrections to the dielectric constant are introduced. The same conclusion applies to the numerical discrete-dipole approximation (DDA) [124–126], within which a particle interacting with light is represented as a discrete set of point dipoles with certain polarizabilities. In the case of ultra-small clusters, only one dipole per cluster can be used eliminating the need to assign an effective size to a cluster [127].

EFFECTIVE MEDIUM THEORY The approaches mentioned above are designed to investigate far- and near-field optical properties of individual nanoparticles or assemblies of several of them with particular spatial configuration. But when the amount of particles increases and their number and position become uncertain, these methods can be hardly applied due to extremely high computational costs. For very dilute solutions the assumption of non-interacting particles in the sample can be made. In this case the optical response of an N -particles ensemble is considered to be just N times the response of a single particle, while the latter can be simulated using any appropriate method. Evidently, this assumption is not valid for dense ensembles of nanoparticles and for nanoparticle aggregates. An efficient approach to simulate absorption and extinction of light by samples containing many densely packed nanoparticles with the size of an individual constituent much smaller than the wavelength is the effective medium theory. Within this approach a real medium consisting of a solvent or solid matrix with numerous embedded nanoparticles is represented by an effective medium with a dielectric constant modified to reproduce the optical response of the real system [6]. The contribution of Maxwell Garnett [128, 129] can be considered as a pioneering work in this field, in which he proposed the dielectric function of the effective medium optically equivalent to a low-volume-fraction dispersion of randomly placed metal particles. Other authors proposed different effective dielectric constants to describe dispersions with high volume fractions of metal particles, including those with metal particles distributed inhomogeneously over an embedding medium [130].

QUASI-STATIC APPROXIMATION Since the size of a noble-metal cluster usually does not exceed 1% of the wavelength of the incident light, the electrodynamics treatment of the light-matter interaction problem can be commonly replaced with the electrostatic one [127, 130], which is usually called the quasi-static approximation. In this regime an external electric field is considered to be time-dependent, but spatially uniform over a single particle. The difference to the conventional electrostatic approach lies in using of frequency-dependent dielectric constants for the particle and the surrounding medium. The quasi-static approximation can be used to study the optical properties of structured aggregates of metal clusters as well as their solutions or dispersions. In this case each particle is considered as a point dipole or higher-order multipole emitter and the electric field acting on each sub-unit is represented by the sum of an external electric field and the fields scattered by all other members of the aggregate. The final configuration of the electric field is determined in a self-consistent manner [130].

As has been shown, the important prerequisites for the well-established classical-electrodynamics methods are dielectric constants or polarizabilities and in some cases geometric radii of nanoclusters. If the size of a cluster is below ~ 10 nm, additional corrections to the dielectric constant are required, which reflect the electron confinement. Some approaches exist, which introduce these corrections based solely on classical considerations, such as limited electron mean free path or soft boundaries [130]. These corrections predict the R^{-1} dependence of the dielectric constant on the cluster radius. Evidently, this result leads to an unphysical increase of the permittivity at atomic sizes, which must be finite for atoms. Unfortunately, other approaches to introduce this size correction involving quantum-mechanical models lead to the R^{-1} dependence as well and are therefore inapplicable to ultra-small noble-metal clusters.

III.2 *Mixed quantum-classical methods*

Another way to overcome the difficulty with the proper size dependence of the dielectric constant of molecular-like systems is to employ the quantum-mechanical methods directly to describe electric field-driven electron dynamics in a nanocluster and couple this quantum-mechanical system to the classically described external electromagnetic field. This approach has been successfully implemented in studies of optical properties of molecular systems placed in the close vicinity of a nanoparticle or their aggregate [131–135].

Within the method developed by Girard *et al.* [131, 132], the strongly-nonuniform electric field produced by an aggregate of nanoparticles and experienced by a molecule, is represented in terms of a non-local electric field susceptibility tensor. The temporal evolution of the molecular system is described using the Liouville equation for the density matrix with the Hamiltonian in-

cluding this external electric field. The rotating wave approximation allows for reducing the Liouville equation to the set of optical Bloch equations and ultimately to simulate the fluorescence signal of a molecule. This approach can be straightforwardly applied to investigate scattering, absorption or fluorescence properties of metal nanoclusters, but not of their assemblies, since it does not take into account the effect of the quantum system on the resulting electric field and, therefore, cannot describe the cluster-cluster interaction. Moreover, it is limited only to two-level systems, which is not sufficient if such optical properties as lasing are of interest or if the realistic description of a cluster is required.

Another group of hybrid quantum-classical methods [133, 134, 136] rests upon the decomposition of the total electric field into a "macroscopic" contribution due to a plasmonic nanoparticle and a "molecular" one which arises due to a molecular system. Both of these fields are governed by the classical Maxwell equations. The current density in the nanoparticle is derived as the response to the total electric field, while the molecular current density is determined by solving the optical Bloch or Liouville equations under the action of the "macroscopic" electric field. In this manner, the optical response of a molecular system is governed by an external electric field created by a nanoparticle, which on its turn is affected by a molecular system. Usually, for the "macroscopic" electric field such numerical methods as FDTD or FEM are used, while for the properties of interest of the "molecular" system semi-analytic expressions are derived, which again limits the applicability of the approach to two- or three-level quantum systems.

III.3 *Quantum mechanical description of the optical properties*

In the size regime where "each atom counts" a metal nanocluster can be treated as a regular molecule. Hence, the well-developed methods of quantum chemistry (QC) can be used to simulate its optical response. One of the most popular and widely used QC methods for the investigation of the ground-state properties of moderate- and large-sized molecules is the density functional theory (DFT) [137–140]. The essence of this approach lies in the substitution of a real many-electron complex system by a reference one consisting of non-interacting electrons in a one-particle potential, known as the Kohn-Sham potential. The latter is defined by the constraint that the electronic density of such a reference system in this potential should coincide with the electron density of the real system under consideration. Thus when this one-particle potential is determined, the ground state properties of the real system can be calculated in an ultimately simple and fast manner. Unfortunately, the exchange-correlation potential which is a part of the Kohn-Sham potential, can not be exactly determined for an arbitrary system and thus in general has to be approximated.

For this purpose, in recent decades numerous exchange-correlation functionals have been developed [141–145] aiming to cover a wide range of molecular systems and to reproduce different properties of them [146–148].

Regarding the optical response, especially absorption of light, of ultra-small metal clusters, not only the ground state but also the excited state properties need to be simulated. A valuable tool for the calculation of the excited state properties of molecular systems is the time-dependent DFT (TDDFT) [149–152], which is an extension of the density-functional approach to time-dependent problems. It can be shown that there is a one-to-one correspondence between a time-dependent electron density and time-dependent external potential, which implies that the electron density of an artificial system of non-interacting electrons placed in a time-dependent Kohn-Sham potential is evolving exactly as the many-body interacting system in an external potential [149]. This simple approach grants the possibility to calculate not only excited state energies and intensities of the corresponding transitions, but also excited state geometries, dipole moments, vibration frequencies, *etc.* In general, TDDFT allows for treating relatively large systems at reasonable computational cost with satisfying accuracy, provided that the exchange-correlation functional is properly chosen [153, 154]. Some properties like Rydberg states, charge transfer states, conical intersections, or double excitations are poorly reproduced by TDDFT [155–157], but new functionals and corrections are constantly being developed [145, 158] to overcome these problems. In some sense, TDDFT bridges the accuracy of *ab initio* quantum-chemical methods which are derived from the first principles of quantum mechanics with the efficiency of semi-empirical ones which employ some parameters determined based on experimental data.

Besides the density-based methods, numerous many-body wave-function-based approaches have been developed and employed to describe the ground and excited state properties of the noble-metal clusters. The cornerstone of these methods is the well-known Hartree-Fock (HF) method [159] which allows one to obtain an approximation to the electronic ground state energy and wavefunction. Within the HF approach the many-electron wave-function is represented as a product of single-particle functions (spin-orbitals) antisymmetrized with respect to the exchange of any pair of electrons, which is known as the Slater determinant. The optimal set of spin-orbitals which provide the minimal electronic energy expectation value is determined in a self-consistent manner. Since the HF method is based on the variational principle, it provides an upper bound to the electronic energy of the lowest-energy electronic state of given symmetry and multiplicity. In most cases the ground state of a molecule is of interest. The weakness of the HF method is the neglect of the correlation between electrons with antiparallel spins, which leads to a discrepancy between the real ground state energy and the HF energy.

To overcome this difficulty, numerous approaches known as post-HF methods have been developed which employ the HF wave-function as the starting point and differ in the way they make corrections to it to improve the description of the molecule's ground state. Among these methods the configuration interaction (CI) and coupled-cluster (CC) methods, many-body perturbation theory (MBPT), and multi-configurational self-consistent field (MCSCF) approach should be mentioned [159]. The fundamental idea of both CI and CC lies in the representation of the ground state wave-function as a combination of the ground and multiply excited Slater determinants including all possible excitations of electrons between spin-orbitals. Evidently, the full expansion is computationally prohibitive for almost all systems except the smallest ones, therefore different truncation schemes have been developed to make these approaches more practicable. Among the schemes based on the CI expansion, CI with only single electron excitations (CIS) [160], and CIS with perturbative correction to account for double excitations (CIS(D)) [161] should be mentioned. In its turn, CC gave rise to a vast hierarchy of approximations, such as CC2 [162], CCSD [163], CCSD(T) [164] and many others. The MCSCF approach on its turn demands optimization not only of expansion coefficients of the multi-configurational ground-state wave-function, but also of the molecular orbitals themselves. It is evident, that the flexibility of the trial wave-function within the post-HF methods allows for obtaining much more accurate results, but at the same time makes them computationally impractical even for moderate-sized molecules. However, applying the linear-response (LR) [165] or equation-of-motion (EOM) [166] formalisms to the truncated CC approximations resulted in accurate approaches for the simulation of excited state properties. These approaches, although more computationally expensive than linear response TDDFT, can serve as references to which the TDDFT results can be compared or can be used for simulations of systems and properties in cases when TDDFT fails.

IV METHODS FOR SIMULATION OF COUPLED ELECTRON-NUCLEAR DYNAMICS IN NANOCCLUSERS

Various experimental techniques were developed in order to interrogate the electronic and structural rearrangements in metal nanoclusters under the action of external laser fields. One of the most widely used approaches is the pump-probe method. The essence of this method can be briefly divided into two steps: First, a pump pulse launches dynamical processes in an ensemble of mass-selected metal clusters. Second, a probe pulse interacts with the ensemble resulting in some observable signal, which is detected in the experiment. If the observable is sensitive to the instantaneous electron-nuclear configuration, then by varying the time delay between the pump and probe pulses one can

obtain a time-dependent signal, which carries the fingerprint of the occurring dynamical process. The observables measured in this kind of experiments typically are photoelectron kinetic energies and their angular distribution, molecular fragmentation or ionization yield, and fluorescence intensity [110, 167–171]. Therefore, it is the goal of theoretical simulations to establish a correspondence between various ultrafast observables detected in femtosecond time-resolved experiments and the underlying nuclear and electronic dynamics and to interpret the obtained results [95, 172–174]. Another challenging task for theory is to propose new possible observables, which might be more sensitive to a specific dynamical process and can be measured in a pump-probe scheme, thus inspiring new experimental developments.

One of the cornerstones of the simulations of coupled electron-nuclear dynamics in molecular systems is the Born-Oppenheimer approximation [175], which turns to advantage the tremendous difference between the electron and nuclear masses and thus the characteristic time scales of dynamical processes. It allows for the separation of electronic and nuclear coordinates in the molecular Hamiltonian and considering the electronic motion in a potential parametrically dependent on the nuclear configuration. Simultaneously, the nuclear dynamics is governed by a potential arising from the current nuclear and electronic configuration. The breakdown of the Born-Oppenheimer approximation is observed when two electronic eigenstates closely approach each other, for instance, in the vicinity of a conical intersection or avoided crossing. In this case the interrelation between electronic and nuclear coordinates known as nonadiabatic coupling starts to play an important role, leading to such phenomena as radiationless decay.

The separation of the dynamics into two different processes suggests also the possibility to treat them at distinct levels of theory appropriate for each separate subsystem and to couple them afterwards. This idea constitutes the basis of the numerous MD methods, where the nuclear motion is treated classically as occurring on a precalculated multidimensional electronic potential energy surface (PES). The relevance of this approach for noble-metal clusters can be illustrated, for instance, on the example of Ag_3 , where the linear non-equilibrium geometry of the neutral species has been experimentally created by electron photodetachment from the anionic cluster Ag_3^- and the geometry relaxation in the neutral ground state has been studied [176]. As the observable signal used to study relaxation dynamics, the positive-ion yield obtained after a second time-delayed photoionization process has been employed. The quantum-classical simulations involving the propagation of classical trajectories on precalculated electronic ground-state PES of the neutral cluster [177] demonstrated good agreement with the experimental data and have been further supported by quantum-mechanical simulations of the nuclear wavepacket

dynamics in the laser-field-coupled PES of the anionic, neutral, and cationic species [91].

Calculation of the full PES for a complex system containing many vibrational degrees of freedom is feasible only for relatively small clusters containing no more than few atoms. Aiming to extend the applicability of molecular-dynamics methods to larger systems, the *ab initio* MD “on the fly” in the frame of DFT has been proposed [178, 179], which does not require precalculated PES. Instead, the essence of the MD “on the fly” approaches consists in the propagation of the nuclear trajectories in parallel with quantum-chemical calculations of electronic energies and their gradients only for those nuclear configurations traversed at the given instant of time. Therefore, the method can treat molecular systems in their full complexity without the restriction only to several selected nuclear degrees of freedom or to very small systems.

The investigation of relaxation processes occurring in metal clusters demands the inclusion of a large number of excited electronic states together with the ground electronic state and to account for the nonadiabatic coupling between all these states. Within semiclassical MD approaches this goal can be achieved by following the Ehrenfest mean-field scheme [180], in which the classical nuclear trajectory is propagated in an effective potential, represented by a combination of adiabatic electronic potentials weighted by an electronic population of the respective electronic energy states obtained from solving the time-dependent Schrödinger equation (TDSE) for the electronic degrees of freedom along the nuclear trajectory. Another popular approach is the trajectory surface hopping method introduced by Tully [181], in which every classical trajectory is propagated in a particular electronic state and is allowed to “hop” to a different state stochastically depending on the time-dependent populations of the electronic states. The average over the ensemble of trajectories then provides an approximate description of the full quantum mechanical coupled electron-nuclear dynamics. Compared to the Ehrenfest approach, the surface-hopping procedure is advantageous for simulation of the relaxation processes in metal nanoclusters due to the proper asymptotic behavior of the ensemble of trajectories in regions where electronic states are weakly coupled.

One of the most important ingredients needed for the simulation of ultrafast pump-probe experiments is the coupling between a molecular system and an external pump laser field, which actually induces the dynamical processes interrogated afterwards by a probe pulse. Inclusion of the electric field directly into the MD simulations is of extreme importance for gold and silver clusters, since besides the energetically well-separated 6s-derived excited electronic states a manifold of dense 5d-derived states is present in the energy spectrum of these clusters and thus competitive population processes to several excited electronic states are highly probable. The external laser field has been recently introduced into the MD simulations in the frame of the field-induced

surface-hopping (FISH) method [182–184]. This method combines the classical propagation of a swarm of nuclear trajectories in a manifold of electronic states with a quantum mechanical description of the electronic state populations including the interaction with an external laser field. Similar to Tully's surface hopping procedure, the individual trajectories are allowed to switch their electronic state stochastically according to transition probabilities derived from the electronic state populations. In principle, the FISH method can be coupled to any quantum-mechanical approach for electronic structure calculations, provided the ground and excited state electronic energies, nonadiabatic couplings and transition dipole moments between all the states can be efficiently computed. Among the numerous electronic structure methods, TDDFT has proven its wide applicability for noble-metal clusters, since it represents a balance between accuracy and efficiency. Moreover, an approach to obtain approximate nonadiabatic couplings and transition dipole moments within TDDFT has been recently proposed [185]. Therefore in the current work the FISH method combined with TDDFT is used for the simulation of coupled electron-nuclear dynamics.

V THE STRUCTURE AND GOALS OF THE THESIS

One of the goals of the present thesis is the investigation of the dynamical processes induced in small noble-metal clusters by femtosecond laser pulses. Parallel to the dynamics, ultrafast observables such as photoelectron or high-harmonic signals are simulated. This allows, in the first case, for comparison between the theoretical and experimental data to verify the theoretical conclusions and in the second case, for proposing the high-harmonic signal as a novel promising observable to be measured in the pump-probe experiments. The second goal of the thesis is the development of methods to simulate the exciton propagation in ordered arrays constructed of small noble-metal clusters and to investigate the possibility to control this process.

The thesis is structured as follows: In Chapter 1 the ultrafast coupled electron-nuclear dynamics in small silver clusters induced by external laser fields is investigated and a high-harmonic generation (HHG) signal is proposed as a new promising observable for the femtosecond pump-probe experiments. The HHG in molecules became the subject of intense studies recently, and the experiments reported demonstrated the high sensitivity of the emitted harmonic spectra to the nuclear configuration [186, 187]. With regard to the ultra-small noble-metal clusters, it was demonstrated, that efficient HHG is possible in such systems upon excitation even with laser pulses of moderate intensity, if these are resonant to an intense optical transition [188]. The ensuing dynamical processes should strongly affect the HHG emission signal. Chapter 1 is devoted to the investigation of this process on the example of the Ag₂

and Ag_8 clusters. First, the coupled electron-nuclear dynamics in these clusters is simulated in the frame of TDDFT using the mixed quantum-classical FISH approach [182], which is also described in detail in this Chapter. It is demonstrated, that Ag_8 clusters undergo ultrafast isomerization in the excited state on the sub-picosecond time scale. Second, the method is developed to simulate the HHG signal in the small metal clusters under the action of laser pulses of moderate intensity. The method is applied along the nonadiabatic dynamics to demonstrate the sensitivity of the HHG signal to the instantaneous electron-nuclear configuration of the clusters. It is shown, that indeed the time-resolved HHG spectrum carries the fingerprints of the vibrational nuclear motion in the both ground and excited electronic states and can be employed for interrogation of the non-adiabatic processes in molecular-like noble-metal clusters.

Chapter 2 is devoted to a systematic investigation of solvation effects on the dynamical processes taking place in small anionic gold clusters upon photoexcitation. The theoretical studies were motivated by the experiments performed in the group of Prof. Gerd Ganteför at the Physical Department of the University of Konstanz. By means of time-resolved photoelectron spectroscopy (TRPES) it was found, that the fragmentation of an anionic Au_3^- cluster occurred on different time scales or could be even quenched depending on the number of water molecules adsorbed to it [96]. The theoretical investigations of the underlying processes have been carried out involving the coupled multistate electron-nuclear dynamics simulations in the frame of the FISH method. The simulations reveal that there are two competing processes in the Au_3^- clusters arising upon photoexcitation, namely, the non-radiative relaxation to the ground state and the cluster dissociation in the excited state. It is demonstrated, that these two processes take place on different time scales determined by the number of attached water molecules, which opens a possibility to steer the photofragmentation processes of ultra-small noble metal clusters by the controlled adsorption of water molecules. The simulated TRPES signal of the cluster ensemble as well as the traces of fragments are in a very good correspondence with the results of measurements, thus supporting the proposed theoretical explanation.

Additionally, in Appendix A another relaxation mechanism occurring in small anionic gold clusters is studied both theoretically and experimentally using femtosecond time-resolved photoelectron spectroscopy (TRPES) and non-adiabatic dynamics simulations in the frame of TDDFT. The theoretical investigations were motivated by the experimental findings obtained by the group of Prof. Wolfgang Eberhardt and Dr. Matthias Neeb at the Helmholtz-Zentrum of Berlin. Experimentally, it was observed, that the temporal evolution of photoelectron spectra of the Au_7^- cluster upon excitation with a 3.12 eV pump pulse is substantially different from the one previously observed with 1.56 eV pump pulse excitation [102]. Evidently, the two pump pulses with different photon energy initiated different dynamical processes in the cluster ensemble. To get

insight to this effect, simulations of coupled electron nuclear dynamics have been carried out in the frame of the FISH approach. Additionally, TRPES of the Au_7^- ensemble were calculated along the dynamics and compared to the measured ones. The agreement between the theory and experiment is very good, which ensures that the simulations properly describe the dynamical processes occurring in the ensemble at the femtosecond time scale. The theoretical investigations demonstrate, that two types of electron-nuclear dynamics can be initiated in small noble-metal clusters depending on the pump pulse photon energy. With low-photon-energy pump the low-lying well-separated electronic states are populated, and subsequent energy transfer to the nuclear vibrational degrees of freedom leads to cluster isomerization and melting [102]. In contrast, the high-photon-energy pump pulse excites the higher-lying dense manifold of electronic states, in which fast electronic relaxation occurs without any noticeable energy redistribution between the electronic and nuclear degrees of freedom. Thus it was demonstrated that in ultra-small noble-metal clusters both molecular-like and bulk-like coupled nuclear-electron dynamics can be induced by variation of the pump pulse photon energy.

The second part of the thesis, the Chapters 3 and 4, presents the results of simulation and control of light propagation in structured arrays consisting of noble-metal nanoclusters. The research was inspired by the impressive results on plasmon propagation, localization and control in large plasmonic nanoparticles as described in Sec. 1.3. It is evident, that the theoretical methods used to simulate the plasmon propagation in nanoparticle aggregates, reviewed in Sec. III.1, are not applicable to molecular-like metal clusters due to the small size of the latter. Within the mixed quantum-classical approaches described in Sec. III.2 the quantum object is treated as a two- or three-level system. This is not sufficient for the realistic description of noble-metal cluster aggregates, in which the intercluster coupling is expected to cause the population transfer to excited electronic states other than the one resonant to the external field. Therefore a method was developed to simulate the electron population dynamics and exciton propagation in ordered noble-metal cluster arrays under laser pulse excitation. This method, which is presented in Chapter 3, couples TDDFT for a realistic description of the electronic structure of each single cluster to a fully-quantum-mechanical treatment of the array evolution in an external electric field and to the classical evaluation of the electric field produced by the array. Additionally, in Chapter 3 a quantum-classical approximation to this method is developed, which allows for simulation of light propagation in large arrays with many electronic states per cluster taken into account. Within this approach the quasi-static approximation for the scattered electric field and the cluster-cluster interaction is combined with the time-dependent Schrödinger equation (TDSE) for a single cluster solved in the manifold of TDDFT electronic

states. The theoretical methodology is applied to study the optical response of Ag_2 and Ag_8 cluster arrays to an external resonant laser pulse excitation.

In Chapter 4 the developed methodology applied to demonstrate the possibility to control the exciton propagation in such ultra-small metal cluster arrays. A genetic algorithm is used to determine the parameters of a phase-modulated laser pulse irradiating a T-shaped structure built up of seven Ag_8 clusters. Each species within a generation is represented by a single simulation of light propagation in this structure under the action of a pulse with particular phase parameters. The target function for the pulse optimization is constructed as the ratio of field energies localized at individual clusters in different parts of the array at the final stage of the simulation. After ca. 30 generations the optimal parameters of the laser pulses, driving the excitation in two different directions, are determined. Employing the two optimized pulse shapes, the electron population dynamics in the array is studied and the underlying mechanism is discussed.

Finally, in Appendix B the developed theoretical approach is extended to include the effect of a substrate into the simulations. Unlike the large conventional nanoparticles, the interaction of metal nanoclusters with the support can dramatically change their optical properties. Among the expected effects are the nuclear rearrangement and reorganization of the ground and excited state electronic structure. These effects are taken into account in the single-cluster TDDFT calculations. Additionally, upon the inclusion of the support in the simulation, the size of an individual subunit can not any longer be considered to be much smaller than the separation between the subunits. Thus, a method beyond the dipole-dipole approximation is required to describe the coupling between the individual subunits. The partial transition charge method [189] allows to overcome this difficulty and therefore is utilized to extend the theoretical approach presented in Chapter 3. It allows for taking into account the interactions of multipolar orders higher than the dipole-dipole one. The modified theoretical method is further used to study the electron dynamics in a flat ring structure built up of ten porphyrin- Ag_4 subunits under the action of a circularly-polarized pulse. The simulations demonstrate, that the left- and right-hand polarized laser pulses give rise to different optical response of the ring, thus allowing to discriminate between the rotation directions of the polarization plane using the metal-cluster-based aggregates and to control the electric field localization in such structures.

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Chapter 1

SIMULATION OF LASER-INDUCED COUPLED ELECTRON-NUCLEAR DYNAMICS AND TIME-RESOLVED HARMONIC SPECTRA IN COMPLEX SYSTEMS

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Chapter 2

EXCITED STATE NONADIABATIC DYNAMICS OF BARE AND HYDRATED ANIONIC GOLD CLUSTERS $\text{AU}_3^- [\text{H}_2\text{O}]_n$ ($n=0-2$)

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Chapter 3

AB INITIO SIMULATIONS OF LIGHT PROPAGATION IN SILVER CLUSTER NANOSTRUCTURES

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Chapter 4

OPTIMAL CONTROL OF LIGHT PROPAGATION IN ARRAYS OF MOLECULAR-LIKE NOBLE-METAL CLUSTERS

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CONCLUSIONS AND OUTLOOK

In the first part of the present thesis, the multistate coupled electron-nuclear dynamics in nanosized noble-metal clusters is theoretically investigated employing the mixed quantum-classical FISH method. Several different relaxation processes induced by photoexcitation are observed and studied. It is demonstrated that the mechanism of electron-nuclear relaxation in the small Ag_8 cluster involves significant nuclear rearrangement occurring on the sub-picosecond time scale, which leads to lowering of the cluster symmetry and noticeable reorganization of the electronic energy level structure. This isomerization is accompanied by electronic relaxation to the lower-lying excited states. However, no substantial electron population transfer back to the ground state is observed within 2 ps of the simulation time.

The relaxation processes observed in the Au_3^- cluster occur within a much longer time scale due to the large energetic separation between the electronic states. Within 1 ps of the simulation time the electron-nuclear dynamics involves the vibrational nuclear motion and concomitant minor decay to the lower-lying electronic excited states. According to the experimental measurements, the electron-nuclear relaxation leads ultimately to the fragmentation of the cluster into Au_2 and Au^- or into Au_2^- and Au . This process occurs on the nanosecond time scale and therefore is beyond the reach of the current theoretical approach.

Essentially faster occurs the relaxation in the Au_7^- cluster at high excitation energies, when the cluster is initially promoted to the dense manifold of 5d-derived electronic states. In this case the electron-nuclear dynamics involves mainly the ultrafast electronic relaxation within this manifold of states. Within a simulation time of 1 ps the nuclear rearrangement remains insignificant, which is characteristic to relaxation processes occurring in bulk materials rather than in molecules.

The effect of solvation on the nonadiabatic electron-nuclear dynamics is investigated on the example of $\text{Au}_3^-[\text{H}_2\text{O}]_n$ ($n=0\dots 2$) complexes. The simulations reveal, that upon adsorption even of a single water molecule, the relaxation time of the anionic gold cluster is dramatically decreased down to picoseconds. The reason is, that the hydrated clusters possess a higher density of electronic states as compared to the bare Au_3^- cluster, which reduces the relaxation time within this manifold of states. The coupling to the nuclear degrees of freedom leads to nuclear rearrangement. As a consequence, the energy gap between the ground and excited states becomes smaller and nonradiative relaxation to the ground state occurs. Therefore, an increasing number of adsorbed water molecules results in faster relaxation times, which is supported by the experimental findings.

Another interesting property of the Au_3^- is the existence of a weakly-bound low-lying electronic excited state. The character of this state does not change upon water molecule adsorption. If the cluster resides long enough in this

state, it can be fragmented into Au_2 and Au^- or into Au_2^- and Au , which is observed both experimentally and theoretically for Au_3^- and $\text{Au}_3^-[\text{H}_2\text{O}]$. In contrast, no fragmentation of Au_3^- clusters with more than one adsorbed water molecule is detected. This is explained by a competing process which occurs in the Au_3^- cluster upon photoexcitation, namely, nonradiative electron-nuclear relaxation. Since the fragmentation takes place in the weakly-bound excited state, it becomes essential how long the cluster remains in this state. With two or more water molecules adsorbed, the nonradiative relaxation occurs on much faster time scale, thus suppressing the photofragmentation.

Parallel to the nonadiabatic dynamics simulations the ultrafast observables, which can be measured in time-resolved pump-probe experiments, are calculated. For the bare and solvated Au_3^- cluster as well as for the Au_7^- cluster the TRPES signal is simulated and compared to the experimentally measured one. The correspondence between the theoretical and experimental TRPE spectra in both cases is very good, confirming the theoretical conclusions on the multi-state nonadiabatic dynamics in these clusters. In the case of the Ag_8 cluster the time-resolved HHG spectrum is simulated to demonstrate the sensitivity of the HHG signal to the instantaneous electron-nuclear configuration. For this purpose, the necessary theoretical methodology is developed. The simulations reveal, that the time-resolved HHG spectrum of the Ag_8 cluster carries bright fingerprints of the photo-induced isomerization process, occurring in this cluster. On the example of the benchmark Ag_2 cluster it is shown, that the HHG spectrum reflects not only the deviation of nuclei from an equilibrium position, but also the direction of their motion. As a result, the time-resolved HHG spectrum is proposed as a promising observable for the ultrafast pump-probe experiments.

In the second part of the thesis, light propagation and exciton transfer in structured aggregates consisting of noble-metal nanoclusters are investigated. As the first step, a method to model the light propagation in the metal-cluster arrays is developed. This involves the calculation of the electronic excited state energies and full transition dipole moment matrix for each single cluster in the array, the construction of the excitonic Hamiltonian for the whole array assuming dipole-dipole interaction between the clusters, and the propagation of the TDSE in the manifold of the Hamiltonian eigenstates under the action of an external electric field. As a result of the quantum-mechanical calculations, the time-dependent dipole moment of each sub-unit in the array is determined and further employed in the classical-electrodynamics evaluation of the time- and spatially-dependent electric field produced by the array. In order to validate the method, the absorption spectra of a pair of Ag_2 dimers, obtained from the excitonic Hamiltonian are compared to the ones calculated using the correlated CC2 method for the whole system. The results demonstrate, that the

dipole-dipole coupling between clusters allows for an accurate description of such systems.

Since the size of the Hamiltonian matrix grows exponentially with the number of clusters in the array, the method becomes computationally prohibitive even for arrays of moderate size, especially when a large number of electronic excited states per cluster needs to be taken into account. Therefore, to treat large arrays with many energy states per cluster, an approximate method is proposed, in which the interaction of each single cluster with the external electric field as well as with other clusters in the array is considered in a self-consistent manner, requiring an iterative procedure to solve the TDSE for each single cluster separately. The developed approximation is compared to the full-quantum treatment on the example of silver cluster dimers and the range of its applicability is discussed.

This approximate method allowed for the simulation of the optical response of a T-shaped array consisting of seven Ag_8 clusters. In order to describe the clusters' electronic structure realistically, 100 excited electronic states per cluster need to be taken into account. Evidently, the full-quantum treatment of this system is beyond the potential of modern computers. Employing the developed iterative approach combined with a genetic algorithm, two different phase shapes of the external laser pulse have been determined, driving the exciton to a selected cluster in the array. Thus the possibility to control the light propagation in arrays constructed of ultra-small noble metal clusters is demonstrated for the first time.

Finally, the methodology developed for the simulation of electron dynamics and light propagation in metal nanoclusters is extended to include the effect of a substrate in the simulations. Due to the small size of the clusters considered here, the interaction with the support leads to noticeable changes in their nuclear and electronic configuration. In order to take this rearrangement into account, the cluster together with a part of the supporting material is considered as a unit building block of the array. To apply the formalism developed for the arrays with well-separated clusters, the description of the coupling between neighboring sub-units is improved. Reciprocally to the transition charge approach developed to describe the Coulomb interaction between biochromophores, where the size of molecules exceeds the separation between them, the transition-charge-based interaction between the array sub-units is introduced. It allows for inclusion of higher multipolar terms in the interaction. The improved method is applied to demonstrate the chiral properties of a ring structure built up of ten porphyrin- Ag_4 sub-units. In this model system the porphyrin molecules play a role of a substrate, on which the metal cluster array is deposited. The simulations demonstrate, that the electron dynamics and near-field distribution are significantly different for two different rotational directions of the polarization plane of the exciting laser pulse.

The results of investigations presented in the thesis can perform as a starting point for further theoretical and experimental developments in several directions. First, the time-resolved HHG measurements in noble-metal clusters are strongly desirable not only to provide insight into coupled electron-nuclear dynamical processes occurring in the clusters, but also to supply with a feedback required to improve the theoretical approach. Second, the theoretical methodology developed for simulation and control of light propagation and exciton transfer in nanosized metal-cluster arrays might motivate experimental investigations of these processes with ultimate goal to design ultra-small optical transmission lines, switches, and logical devices constructed on the basis of noble-metal clusters.

Appendix A

SWITCHING FROM MOLECULAR TO BULK-LIKE DYNAMICS IN A SMALL GOLD CLUSTER

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Appendix B

FIRST PRINCIPLES SIMULATION OF LIGHT PROPAGATION AND EXCITON DYNAMICS IN METAL CLUSTER NANOSTRUCTURES

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LIST OF PUBLICATIONS

POLINA G. LISINETSKAYA (BORN MAKSIMENKO)

1. M. I. S. Röhr, P. G. Lisinetskaya, R. Mitrić „Excitonic properties of ordered metal nanocluster arrays: 2D silver clusters at multiporphyrin templates“. *J. Phys. Chem. A* **2016**, DOI: 10.1021/acs.jpca.6b04243.
2. P. G. Lisinetskaya, M. I. S. Röhr, R. Mitrić „First principles simulation of light propagation and exciton dynamics in metal cluster nanostructures“. *Appl. Phys. B* **2015**, *122*, 175.
3. P. G. Lisinetskaya, C. Braun, S. Proch, Y. D. Kim, G. Ganteför, R. Mitrić „Excited state nonadiabatic dynamics of bare and hydrated anionic gold clusters $\text{Au}_3^-[\text{H}_2\text{O}]_n$ ($n = 0-2$)“. *Phys. Chem. Chem. Phys.* **2016**, *18*, 6411–6419.
4. P. G. Lisinetskaya, R. Mitrić „Optimal control of light propagation and exciton transfer in arrays of molecular-like noble-metal clusters“. *Phys. Rev. B* **2015**, *91*, 125436.
5. P. G. Lisinetskaya, R. Mitrić „Ab initio simulations of light propagation in silver cluster nanostructures“. *Phys. Rev. B* **2014**, *89*, 035433.
6. J. Stanzel, M. Neeb, W. Eberhardt, P. G. Lisinetskaya, J. Petersen, and R. Mitrić „Switching from molecular to bulklike dynamics in electronic relaxation of a small gold cluster“. *Phys. Rev. A* **2012**, *85*, 013201.
7. P. G. Lisinetskaya, R. Mitrić „Simulation of laser-induced coupled electron-nuclear dynamics and time-resolved harmonic spectra in complex systems“. *Phys. Rev. A* **2011**, *83*, 033408.
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Berlin, den 25.02.2016

Polina G. Lisinetskaya