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Summary of Ph.D. thesis:

Quantum dynamics and control of ultracold molecules in external fields

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The developments of methods for the formation, manipulation, and control of photonic, atomic, and ionic quantum systems have been awarded many Nobel prizes in physics and chemistry. After the revolution in the field of ultracold matter that was started by the discovery of the laser cooling of atoms and the creation of the first atomic Bose-Einstein condensate, nowadays, we are witnesses of the increased interest in the research on ultracold molecules. Molecules are much more complex objects as compared to atoms due to their internal structure of vibrational and rotational states and possible permanent electric dipole moments. Therefore, the creation, manipulation, and control of molecular quantum systems and processes are much more challenging. Nevertheless, fueled by the promise of exciting current and possible future applications, more and more efforts are made to produce and investigate ultracold molecular gases.

The presented thesis is concerned with theoretical studies of the quantum dynamics and control of ultracold molecules in external fields. Particular attention is paid to the indirect methods of the formation of ultracold molecules. Both standard methods have been employed to non-standard systems and new schemes of formation and quantum control have been proposed and investigated. The reported studies involve both theoretical developments and numerical implementations, and applications. Numerical calculations are performed for systems being investigated experimentally or potentially prospective for future experiments.

The state-of-the-art *ab initio* methods have been applied to investigate the electronic structure of molecular systems important for the ongoing or planned experimental and theoretical research at ultralow temperatures. Next, the electronic structure data have been employed in both time-dependent and time-independent studies of molecular dynamics in the number of

projects on the structure, formation, interaction, control, and collisions of ultracold atoms and molecules.

The main achievements of the thesis may be summarized as follows:

The electronic structure of the SrYb molecule has been investigated for the first time and employed to investigate the possibility of forming deeply bound ultracold SrYb molecules in an optical lattice in a photoassociation experiment using continuous-wave lasers, the first reported in the literature investigation of the formation of a polar ultracold molecule from two closed-shell atoms. Photoassociation near the intercombination line transition of atomic strontium into the vibrational levels of the strongly spin-orbit mixed $b^3\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $C^1\Pi$ states with subsequent efficient stabilization into the $v'' = 1$ vibrational level of the electronic ground state is proposed. Ground state SrYb molecules can be accumulated by making use of the collisional decay from $v'' = 1$ to $v''' = 0$. Alternatively, photoassociation and stabilization to $v'' = 0$ can proceed via the stimulated Raman adiabatic passage provided that the trapping frequency of the optical lattice is large enough and phase coherence between the pulses can be maintained over at least tens of microseconds.

The electronic structure of the Rb_2 molecule has been investigated by employing the double electron attachment intermediate Hamiltonian Fock space coupled cluster method restricted to single and double excitations for all electronic states up to and including the $5s + 5d$ dissociation limit at about 26,000 cm^{-1}. The calculation was the first reported in literature application of this recently developed method to generate highly accurate interatomic interaction potentials. In order to correctly predict the spectroscopic behaviour of Rb_2, the electric transition dipole moments, non-adiabatic coupling and spin-orbit coupling matrix elements, and static dipole polarizabilities have also been calculated with the multireference configuration interaction method.

The optimal control theory has been applied to ultracold multi-photon photoassociation. An optimization functional that suppresses atomic excitation and maximizes the formation of molecules has been derived and tested. The optimal control theory has been employed to maximize the efficiency of the non-resonant three-photon photoassociation of ultracold rubidium atoms when the initial state is the thermally populated continuum of scattering states in a magneto-optical trap. Using a linear variant of the Krotov method, we found that at ultralow temperatures a pulse optimized for one initial scattering energy works also for all other collision energies within the thermal ensemble and for the lowest partial waves. Our study is the first application of the optimal control theory properly treating the initial thermal ensemble of the scattering states in photoassociation and our results open the way to the coherent control of binary reactions.

Next, the evolution of the wave packet created in the thee-photon photoassociation was

investigated and a second laser pulse was employed to drive a resonant two-photon transition transferring the excited-state wave packet to the electronic ground state. After analyzing the transition matrix elements governing the stabilization step, the efficiency of the population transfer by using the transform-limited and linearly chirped laser pulses was discussed. Finally, the optimal control theory was employed to determine the most efficient stabilization pathways. We found that the stabilization efficiency can be increased by one and two orders of magnitude when using linearly chirped and optimally shaped laser pulses, respectively.

The electronic structure of the $(LiYb)^+$ molecular ion has been investigated for the first time and the results of *ab initio* calculations have been employed in the scattering calculations. The prospects for the sympathetic cooling of the Yb^+ ion emerged into ultracold gas of Li atoms have been investigated. The rates for the elastic and inelastic due to the radiative charge transfer and radiative association collisions have been calculated. The photoassociation spectra for the one-photon formation of the singlet state molecular ion and for the two-photon formation of the triplet state molecular ion have been evaluated and single molecule photoassociation spectroscopy is proposed. Consequences of the present results for building a quantum simulator emulating solid-state physics with a hybrid system of ultracold Yb ions and Li atoms have been analyzed.

The influence of the non-resonant laser light on the rovibrational structure of open-shell molecules has been investigated. The spectroscopic signatures of this effect in the Rb_2 molecule for transitions from the $X^1\Sigma_g^+$ electronic ground state to the $A^1\Sigma_u^+$ and $b^3\Pi_u$ excited state manifold has been studied. The latter is characterized by strong perturbations due to the spin-orbit interaction. For non-resonant field strengths of the order $10^9\,\mathrm{W/cm^2}$, the spin-orbit interaction and coupling to the non-resonant field become comparable. The non-resonant field can then be used to control the singlet-triplet character of a rovibrational level.

The non-resonant laser light was proposed to be used to engineer the Feshbach resonances in their position and width in polar paramagnetic ground-state molecules. Magnetically tunable Feshbach resonances in such molecules are too narrow to allow for magnetoassociation starting from trapped ultracold atoms. For non-resonant field intensities of the order of $10^9\,\mathrm{W/cm^2}$, we have found the width to be increased by three orders of magnitude, reaching a few Gauss. This opens the way for producing ultracold molecules with sizeable electric and magnetic dipole moments and thus for many-body quantum simulations with such particles.

A new class of highly magnetic and polar molecules consisting of chromium and closed-shell alkali-metal atom has been proposed and investigated. These molecules are examples of species possessing large both magnetic and electric dipole moments making them potentially interesting candidates for ultracold many-body physics studies. Especially, the competition between the magnetic and electric dipolar interactions and the control with external electric and magnetic

fields can be realized and investigated with these molecules.

The interactions of polar alkali-metal dimers in the quintet spin state have been investigated and the formation of deeply bound reaction complexes was demonstrated. The reaction complexes can decompose adiabatically into homonuclear alkali-metal dimers (for all molecules except KRb) and into alkali-metal trimers (for all molecules) with no barriers for these chemical reactions. This means that all alkali-metal dimers in the $a^3\Sigma^+$ state are chemically unstable at ultracold temperatures, and the use of an optical lattice to segregate the molecules and suppress the losses may be necessary. The unique features of the chemical reactions of ultracold alkali-metal dimers in the $a^3\Sigma^+$ electronic state that can be controled with external electric fields have been discussed.

To summarize, the presented thesis concerned theoretical studies of the structure, formation, interactions, quantum dynamics and control of ultracold molecules in external fields. The standard and new schemes of the formation and quantum control have been proposed and investigated for systems being investigated experimentally or potentially prospective for future experiments and pave the way towards the ultimate goal of the full quantum control over molecular systems and processes.