ICFO
Institut
de Ciències
Fotòniques

Parc Mediterrani de la Tecnologia
Avda. Canal Olímpic, s/n
08860-Castelldefels, Barcelona (Spain)
T +34 93 553 4001
F +34 93 553 4000

Maciej Lewenstein
Head of Quantum Optics Theory Group
Institute of Photonic Sciences
Castelldefels (Barcelona) 08660 Spain

Opinion about the PhD Dissertation: Michał Tomza

It is a great pleasure and honor to be a referee for Michał Tomza's thesis. I have supervised more than 25 theses in my life and was a referee for more than 30. Tomza's dissertation is clearly among the best I have ever read. It is also a beautiful and paradigmatic example illustrating the strength of the Polish school of Quantum Chemistry, going back to the times of Prof. W. Kołos.

The thesis is devoted to the studies of "Quantum dynamics and control of ultracold molecules in external fields". The physics of ultracold molecules is one of the hottest and most important areas of the contemporary AMO physics - physics of ultracold matter and physics of control at quantum level, in particular. Several Nobel Prizes were awarded to this field: starting from the prize for Alfred Kastler in 1966, to Hans Dehmelt, Wolfgang Paul, and Norman Ramsey in 1989, to Claude Cohen-Tannoudji, Steve Chu amd Bill Phillips in 1997, to Ahmet Zewail in 1999, to Eric Cornell, Carl Wyman and Wolfgang Ketterle in 2001, to some extend to Tony Leggett in 2003, to Roy Glauber, Ted Hänsch and Jon Hall in 2005, and, last but not least to Serge Haroche and Dave Wineland in 2012.

The first experiments with ultracold atoms dealt with weakly interacting systems, such as atomic Bose condensates. Since the beginning of the XXIst century the focus is on strongly correlated quantum many body systems. Unprecedented control and precision was achieved in few trapped ion systems. Today these systems are extended to much larger size and even more control. Applications of such systems are various: from quantum computers of special purpose (quantum simulators) to quantum precision metrology (clocks, magnetometers, gravimeters) and quantum sensing. The future and emerging quantum technologies will for sure be based to a great part on ultracold quantum matter.

Ultracold molecules play a particular role in these development since in principle they provide richer and more flexible systems, though more difficult to describe theoretically and to control experimentally. Tomza's thesis deals with these problems in a very close relations to and collaboration with the best experimental groups worldwide. Tomza focuses on the problems of formation of ultracold molecules, both by standard methods to non-standard systems, as well as proposing novel methods of ultracold molecule formation.

The thesis is very well written and composed. Needless to say it is based on six seminal papers in the best physical, and chemical physics journals (PCCP, Mol. Phys, Phys. Rev. A (2, but one written by Tomza alone), Phys. Rev. Lett., and Phys. Rev. A - in Rapid

ICFO
Institut de Ciències Fotòniques

Parc Mediterrani de la Tecnologia
Avda. Canal Olímpic, s/n
08860-Castelldefels, Barcelona (Spain)
T +34 93 553 4001
F +34 93 553 4000

Communications). In total Tomza prepared during his studies 11 papers, 9 of which were published. Apart from the six mentioned, there was a one paper in Faraday Discussion, one in J. Chem. Phys, and another Phys. Rev. Lett.

The thesis starts with an introductory chapter on direct and indirect cooling methods and trapping techniques. It includes short subsections on beam decelerators, buffer-gas and sympathetic cooling, Doppler cooling, Sisyphus cooling, and evaporative cooling, as well as on laser induced and magneto-induced association. Magnetic, magneto-optical, electrostatic and electric dipole trapped are presented. In the second part, the Chapter presents basic techniques of quantum control, from control via interference and pump-dump schemes, through adiabatic methods like STIRAP, to optimal control theory. Applications of ultracold molecules are reviewed in the conclusion of the Chapter: from precision measurements and tests of fundamental laws to many-body physics and quantum simulators, and finally quantum (universal) computations.

Chapter 2 presents motivations and objectives of the thesis. The thesis is concerned with theoretical studies of quantum dynamics and control of molecular systems, with focus on formation of ultracold molecules. In particular the thesis deals with

- Photo-association of closed shell atoms (Sr, Ca, Ytb), in particular formation of SrYb molecules (experiments of T. Zelevinsky)
- Photo-association with short laser pulses
- Control of molecular process with non-resonant light
- Ultracold molecules with spin structure
- Hybride systems of atoms and ions (as in experiments of R. Gerritsma on Li and Yb+)

The objectives of the thesis are thus fourfold:

1. To use state of art ab initio methods to study molecules of interest for the current and future experiments.
2. To study interactions and dynamics of photo-association of SrYb molecules and LiYb+ molecular ions.
3. To investigate possibilitity of photo-association by short laser pulses and multiphoton transitions (applied to an example of $Rb_2$)
4. To investigate the influence of nono-resonant field and to propose new schemes for control of photo-associative formation of yultracold molecules with non-resonant fields

The following Chapters describe the original results obtained in the thesis. In Chapter 3 Tomza reports on ab initio methods and calculations of electronic structure of ultracold molecules. He illustrates the applications of the theory to SrYb, $Rb_2$ molecules, and LiYb+ molecular ion. Separate sections are devoted to $^2\Sigma$ (RbSr, LiYb, RbYb, CsYb), Cr-closed shell molecules, and $^3\Sigma$ alkali molecules. These results were presented in detail in paper I and Paper II (parts A and B of the Bibliography) The paper on molecular ions was still in

ICFO
Institut
de Ciències
Fotòniques

Parc Mediterrani de la Tecnologia
Avda. Canal Olímpic, s/n
08860-Castelldefels, Barcelona (Spain)
T +34 93 553 4001
F +34 93 553 4000

preparation at moment of submission of the thesis, even though the results were already obtained and impressive. The results concerning $^2\Sigma$
Cr-closed shell molecules and $^3\Sigma$ alkali molecules were published in papers IV, V, and VI respectively.

Chapter VI uses the results of Chapter III to discuss formation of ultracold molecules by the CW photo-association. Again, different concrete applications have been presented in different publications. Formation of ultracold SrYb molecules in an optical lattice via photo-association spectroscopy is discussed in Paper I. Extremely interesting results of Section 4.3 on formation of ultracold LiYb+ ion await still a publication.
Chapter V is perhaps more speculative, but also extremely creative: here the idea of formation of ultracold molecules by short-pulse photo-association and multi-photon physics is discussed. Using the results on electronic structure, obtained in Paper II, Tomza proposes to apply optimal control theory to photo-associate $Rb_2$ molecules by three photons. The paper is still in preparation, but the results are very promising, and, moreover, they open the whole novel way of thinking about these processes. Section 5.3 discusses optimized two-photon stabilization of the 3-photon associated molecules. Using the results of Paper II and detailed description of Paper III, the author show how to transfer in the mostly stable way photo-associated wave packet to the ground electronic state.

Finally, the chapter VI opens another new direction for ultracold chemistry – using of non-resonant light to control the rotational-vibrational structure, and then to control the position and width of Feshbach resonances in polar molecules. The results employ the electronic structure calculations of Paper II, but the results of Paper IV.

Chapter VII contains a very clear and promising outlook and perspectives. The bibliography is really extensive (400 positions). It includes also the copies of the 6 published papers as Appendices.

This dissertation fulfills all of the necessary condition to be admitted to the further stages of the dissertation process. I should be immediately permitted for public defense.

Rozprawa kwalifikuje sie bez zadnej watpliwosci do dalszych etapów przewodu doktorskiego, i powinna by´c dopuszczona do publicznej obrony

I have no slightest doubts that this thesis and its author deserve the highest possible distinctions (wyróżnienie). The support for this is contained in a separate letter.

Sincerely yours,

Maciej Lewenstein

ICFO
Institut
de Ciències
Fotòniques

Parc Mediterrani de la Tecnologia
Avda. Canal Olímpic, s/n
08860-Castelldefels, Barcelona (Spain)
T +34 93 553 4001
F +34 93 553 4000

Maciej Lewenstein
Head of Quantum Optics Theory Group
Institute of Photonic Sciences
Castelldefels (Barcelona) 08660 Spain

Opinion about the PhD Dissertation: Michał Tomza

As I said it was a great pleasure and honor to be a referee for Michał Tomza's thesis. I have supervised more than 25 theses in my life and was a referee for more than 30. Tomza's dissertation is clearly among the best I have ever read. It is also a beautiful and paradigmatic example illustrating the strength of the Polish school of Quantum Chemistry, going back to the times of Prof. W. Kołos.

This is a seminal thesis, and it should be in my opinion published as a whole. One possibility is J. Phys. B, which publishes the extraordinary theses in a form of a tutorial article, but for Tomza it is better to seek for a more weighted review journal. As an Editor of Reports of Progress of Physics I will invite Tomza to submit a report on progress article based on his thesis.

I have not the slightest doubt that this thesis and its author deserve the highest possible distinctions (wyróżnienie).

Sincerely Yours,

Maciej Lewenstein

Warszawa, May 19th, 2014.

**Evaluation of the Doctoral Thesis of Michał Tomza**

Doctoral Thesis by Mr. Michał Tomza entitled "Quantum dynamics and control of ultracold molecules in external fields", which is submitted to the Department Council of the Faculty of Chemistry, University of Warsaw, in partial fulfillment of the requirements for the degree of DOCTOR OF PHILISOPHY, was prepared under the supervision of Prof. Robert Moszyński, from University of Warsaw, and Prof. Christiane P. Koch, from University of Kassel, Germany. Mr. Tomza studied for his Ph. D within the International Ph.D. Studies in Quantum Chemistry/Theoretical Physics at University of Warsaw and University of Kassel. The thesis contains novel and very interesting scientific results, obtained during several years of research. This material was a subject of several scientific publications that appeared in Physical Chemistry Chemical Physics, Molecular Physics, Physical Review Letters and Physical Review A. It concerns theoretical studies of the quantum dynamics and control of ultracold molecules in external fields. The new schemes of the formation and quantum control of molecules have been proposed and investigated and they pave the way towards the ultimate goal of the full quantum control over molecular processes.

Below I present a brief summary of Mr. Tomza results presented in the Thesis.

Thesis consists of "Introduction" and "Motivation and objective", followed by four chapters containing the main achievements of scientific studies, "Summary and conclusions" and "Bibliography'. Next author incorporated the body of six papers, where he published his original results. "Introduction" contains very compact, clearly written discussion of the cold atom physics, with briefly description of main cooling techniques, cold molecule formation, including photoassociation and Feshbach resonances, various kind of trapping techniques, optical lattices and quantum control. Quantum control schemes are obtained by introducing laser fields to create quantum interference between two reaction pathways. One can control the outcome of the reaction by tuning the phase difference between lasers. This control can be even more subtle if broad band phase shaped fields are used. Or, as proposed by David Tanner and Ronie Kosloff a sequence of laser pulses with appropriate delay may be used to selectively control molecular dynamics. The latter method is called pump-dump scheme, and the best known example in this class is STIRAP. The secret of quantum control is in the proper optimalization of pulse shape and phase. The reward is achievement of cold molecules, which hold a promise of exciting applications. Among them are: ultraprecise measurements, atomic clocks, precision tests of fundamental laws of nature, ultra-cold chemistry, just to name few of them. All of this is mentioned properly in the 'Introduction", which is closed with brief mention of Bose Einstein condensation, many body physics and quantum simulators.

In the following chapter we find context and motivation of the proposed research. The objective of the research is fourfold:

1. study of the electronic structure of the molecular systems relevant for experiment using the state-of-the-art ab initio methods.
2. interactions and dynamics of the ultracold SrYb molecule and $LiYb^+$ molecular ion and their formation by using standard methods of photoassociation.
3. possibility of an effective production of ultracold molecules by using the short-pulse photoassociation with multi-photon transitions driven by shaped laser pulses,

4. investigation of the influence of the non-resonant fields on ultracold collisions and rovibrational structure of open-shell molecules

The latter task leads to new schemes of controlling the formation of ultracold molecules with a non-resonant light

The next four chapters form an essence of the Thesis.

Chapter 3. **Ab initio electronic structure calculations for ultracold molecules.**

This Chapter contains the results of the state-of-the-art ab initio electronic structure calculations for molecular system relevant for the ongoing experiments, including the electronic structure calculations for the SrYb molecule, $Rb_2$ molecule, LiYb+ molecular ion, $^2\Sigma$ molecules, chromium closed-shell-atom molecules, and finally the reactions of the $3\Sigma$ molecules. They are also used in scattering or time-dependent simulations of molecular processes in next chapters. The results of this chapter are described also in publications I and II. Only selected data is included in this chapter, most of the references to the tables and figures are directed to the original papers.

Ab initio electronic structure calculations play a very important role in physics and chemistry of ultracold atoms and molecules. Any reliable theoretical prediction or experimental proposal is not possible without a credible knowledge of the electronic structure. There is a great demand for this kind of calculations and Warsaw Quantum Chemistry Group has a long tradition in this field, since professor Kołos, of which Michał Tomza is through his advisor, prof. Moszyński, a direct successor. This group also created very sophisticated methods that are state of art.

I am not an expert in electronic structure methods, end it would not make sense for me to evaluate the sophisticated character and relevance of detailed approximation used, but I rely on the great expertise and tradition of the Quantum Chemistry Group of prof. Moszyński. Reading a main body of the Thesis I had a feeling of insufficiency when reading about configuration interaction methods, coupled cluster methods or effective core potential, but when I looked at the Review of Modern Physics paper of Monika Musiał and Rodney J. Bartlett I realized that even including Essential Preliminaries would easily doubled the volume of the dissertation, and would not guarantee substantial increase of my understanding of these methods. For specialists all the approximations and even numerical codes used are listed for each particular molecule and this is in my opinion sufficient. The rest of the details are presented in papers. **The main goal of the part of the thesis is to present the basis for the study of dynamical processes discussed in the following chapters.**

First the electronic structure calculations for the ground and excited states of the SrYb molecule is discussed. This work is motivated by the experiment group of prof. Tanya Zelevinsky at the University of Columbia, where the molecular clock for precision measurements is going to be built. Ab initio data are later employed in photoassociation and STIRAP calculations in Chapter 4.2 whereas a detailed description of the results is presented in Paper I. Next are the high-accuracy electronic structure calculations for the ground and excited states of the rubidium dimer. The ab initio data presented here is employed in the time-dependent studies of the multi-photon molecular formation in Chapter 5 and Paper III. A detailed description of the results is presented in Paper II. It is followed by the results of the electronic structure calculations for the ground and excited states of the LiYb+ molecular ion. This work was motivated by the prof. Rene Gerritsma group experiment at the University of Mainz, where they build quantum simulator emulating solid-state physics with a hybrid system of ultracold ions and atoms. Ab initio calculated data is later employed in the scattering and photoassociation calculations discussed in Chapter 4.2. Next there are the electronic structure calculations for the electronic ground state molecules such as RbSr, LiYb, RbYb, and CsYb with the motivation towards the investigation of the control of magnetic Feshbach resonances with non-resonant laser field (details are in Chapter 6.3 and Paper IV), new class of highly magnetic and polar molecules consisting of the chromium and closed-shell alkali-earth-metal or ytterbium atoms which are potentially interesting candidates for the studies of ultracold many-body dynamics in combined external electric and magnetic fields and finally the calculations of the potential energy for the binary interactions of polar alkali dimers in the quintet state of the bimolecular complex with the goal to explore the possibility of reaction barriers that would prevent molecules from reaching the short-range interaction region. A detailed description of the results is presented in Paper VI.

Chapter 4. **Formation of ultracold molecules by cw photoassociation.**

In this chapter author presents results concerning application of continuous wave laser photoassociation.

First he proposes photoassociative formation of SrYb molecules in their electronic ground state using transitions near an intercombination line in the optical lattice. He suggests the following scheme for the photoassociation of SrYb molecules followed by stabilization via stimulated emission: first optical lattice is chosen to optimally compress the pair density of strontium and ytterbium atoms prior to photoassociation, then a photoassociation laser, red-detuned from the intercombination line transition and resonant with an electronically excited vibrational level is switched on. Next it is turned off while the the stabilization laser is switched on, in order to transfer population to the first excited vibrational level of the $X^1S^+$ electronic ground state, $v_{00} = 1$. Finally molecules decay to the vibronic ground state. Alternatively, photoassociation and stabilization to $v_{00} = 0$ can proceed via 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 next problem considered in the chapter is formation of ultracold $LiYb^+$ ion by photoassociation. The conclusion is that radiative association and radiative transfer should not be a problem for the ultracold $LiYb^+$ formation by using hybrid ion-atom systems based on the Yb+ ion emerged into a gas of the Li atoms. Additionally, because the radiative association dominates the radiative inelastic processes, it can be employed for the formation of the ultracold LiYb+ molecular ions.

Chapter 5. **Formation of ultracold molecules by short-pulse photoassociation.**

In this chapter we find a discussion of optimal control of the femtosecond three-photon photoassociation of ultracold atoms and optimized two-photon stabilization employing potentials with ion-pair character and strong spin-orbit coupling. 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 effciency 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. It is proved 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. Next the evolution of wave packet created in thee-photon photoassociation is analyzed. A second laser pulse is used to drive a

resonant two-photon transition transferring the excited-state wave packet to the ground electronic state. After analyzing the transition matrix elements governing the stabilization step, the effciency of the population transfer by using the transform-limited and linearly chirped laser pulses is discussed. Finally, the optimal control theory is used to determine the most effcient stabilization pathways. The stabilization efficiency can be increased by one and two orders of magnitude when respectively, linearly chirped and optimally shaped laser pulses are applied.

Chapter 6. **Non-resonant light control.**

The last chapter is devoted to the subject of quantum control of molecular processes, which is an ultimate goal of the ultracold physics. Here the author considers the influence of the laser on the molecular rovibrational structure and he comes up with a new schemes of controlling the photoassociative and magnetoassociative formation of ultracold molecules with non-resonant light. First an influence of a non-resonant light on the rovibrational structure is discussed and theory for a diatomic molecule in a spatially degenerate electronic state interacting with a non-resonant laser light is presented. Transitions between the $X^1\Sigma^+_g$ electronic ground state and the $A^1\ \Sigma^+_u$ and $b_3\Pi_u$ excited state manifold in $Rb_2$ molecule in the presence of non-resonant light show that due to strong perturbations caused by the spin-orbit interaction, for non-resonant light of the order $10^9$ W/cm$^2$, the spin-orbit interaction and coupling to the non-resonant field become comparable, and non-resonant field can then be used to control the singlet-triplet character of a rovibrational level.

In the second part of this chapter author considers a non-resonant light control of magnetic Feshbach resonances. It is shown that that the non-resonant light, which universally couples to the polarizability of a molecule, induces Feshbach resonances and modifies their positions and widths in the mixtures of open-shell/closed-shell atoms. It happened because non-resonant light modifies both the background scattering length and the magnetic susceptibility. Using this properties (Feshbach resonance) author examines the possibility of creating ultracold molecules with sizeable electric and magnetic dipole moments. Magnetically tunable Feshbach resonances in such molecules are too narrow to allow for magnetoassociation starting from trapped, ultracold atoms. For non-resonant light intensities of the order of $10^9$ W/cm$^2$, the width of the resonance is increased by three orders of magnitude, reaching a few Gauss.

This is the main contents of the Thesis. In my opinion this is excellent scientific research material and is very clearly presented. I found here pleanty of interesting results and in my opinion this work is more than enough for single Doctor Thesis. As I can see, not all the publications of Mr. Tomza were included in the Thesis, perhaps in order to keep coherence and unity. Both list of publications and studies presented here look very impressive.

Finally I would like to mention few minor defects that I found in the Thesis.
The sentence "The ultracold molecules have a much richer internal structure including rotational and vibrational levels and possible permanent electric and magnetic dipole moments." is out of context. There are some small language errors and misprints but they are just minor defects not worth dwelling on and I would like to stress I value the thesis as a whole very highly.

**Hereby I state that this work fit to serve as a basis for awarding the degree of „Doctor of Philosophy".**

**Having very high quality of the work in mind I would like to recommend that the thesis be awarded with distinction. I enclose, in separate document, my detailed arguments supporting this recommendation.**

Marek Trippenbach

**Recommendation for the dissertation award**

**To recognize exceptional and interesting scholarly work produced by Michał Tomza in his doctoral dissertation entitled "Quantum dynamics and control of ultracold molecules in external fields" I would like to recommend this thesis to be awarded with distinction. In my opinion it is straightforward and easy to justify my recommendation and below I list my most important arguments. They are as follows:**

1. **The nominees' overall academic accomplishments are outstanding.**
2. **Originality and innovativeness; the research presented in the thesis is original, very timely and contributes to the very frontiers of the cold atom physics. Quantum chemistry methods used here are very sophisticated and state of the art.**
3. **Scholarly excellence; in my opinion Michał is genuinely a gifted student with great potential as a research scientist. From my review it should be apparent that I think very highly of Michał Tomza academic and research skills and it seems to me I am not alone in this evaluation. He is inquisitive, motivated, and very creative.**
4. **Significant contribution to the discipline; there is a high demand on the kind of results presented in the dissertation of Michał Tomza. Many leading atomic physics laboratories seem to notice both specific data presented in the thesis as well as the potential and power of the methods used.**
5. **Quality of writing; though English is not the authors mother tongue thesis is well written both from the language and material organization points of view.**
6. **Material presented in the dissertation is enough for more than one Ph. D.**

**The list above is along the line of the "Thesis Reviews and Recommendations for the Award" in most prominent universities worldwide. So I conclude that our candidate could easily be awarded not only by Chemistry Department of University of Warsaw, but he satisfies criteria to be awarded by any good university in Europe or United States.**

Marek Trippenbach