

Project VALID  
(*Vibronically Assisted Light Induced Dynamics*)

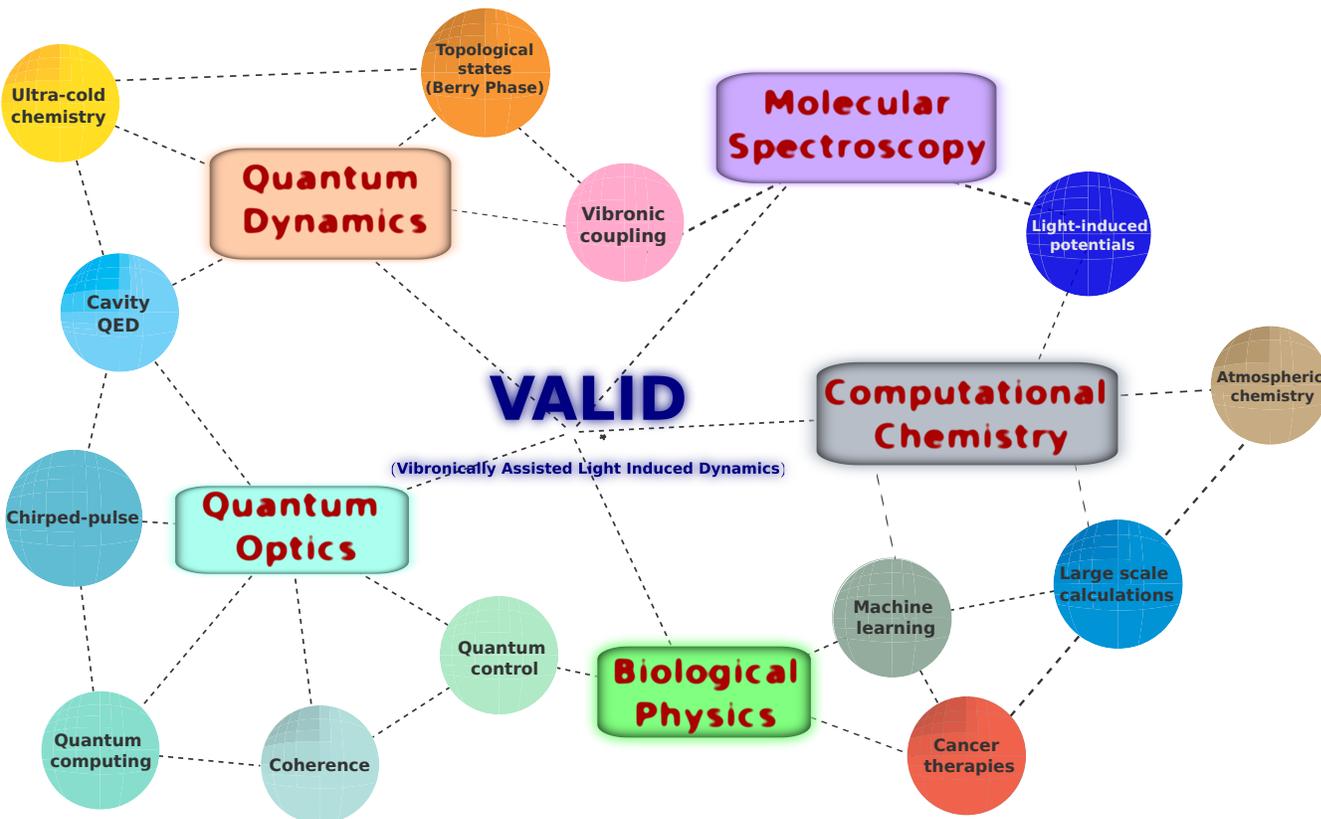
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# 1 Objectives



Project VALID is dedicated to the problem of quantum control of molecules, which are astrophysically, environmentally or biologically significant. The project is interdisciplinary in nature, and aims at networking between researchers of various specialities in chemical physics, molecular quantum optics, medical chemistry and astrophysics.

More specifically, the main goal of the project is a theoretical investigation of non-adiabatic nuclear dynamics in diatomic and polyatomic systems in the presence of tailored electromagnetic fields. Of central interest are intrinsic molecular processes such as photo-dissociation, control of molecular geometry, topological effects, rotational-vibrational relaxation and control of chemical reactions, but also control of molecular translational motion (cooling, trapping) and molecular rotations (alignment, orientation, optical centrifuge).

Considered systems can be divided into two groups. The first group contains small molecules (di- and triatomic, such as  $O_2, LiF, CaF, NO, CO, O_3, SO_2, CO_2, H_3^+$ ), for which accurate quantum-mechanical description is possible and results can be applied to interpret observations from the inter-stellar medium, Earth or exoplanet atmospheric measurements, or high-resolution laboratory spectroscopic data. The second group contains larger molecules, which play a key role in environments of living organisms, for example active centers in proteins present in cancer cells or porphyrine based photosensitizers used in photodynamic therapies. The latter group requires a mixed quantum-classical description.

Although primarily theoretical, the present project is strongly embedded in the experimental context. Collaborations with a number of world's leading experimental groups in chemical physics is a priority pathway to fulfil objectives introduced here, thus to reach an overall success. On the theory side, the basic idea behind the present project is utilisation of powerful tools of theoretical spectroscopy in a synthetic interdisciplinary approach. Many such tools has not been yet widely recognized in fields other than molecular physics.

The project has a three-fold dedication. Primarily it is targeted at explaining observed physical phenomena in small molecules, which are put under the influence of strong external fields. The level of the underlying theory corresponds to high-resolution molecular spectroscopic quantum calculations, which until now were restricted only to the narrow discipline of simulations of rotational-vibrational infra-red spectra from first principles. Tools used successfully in the nuclear motion theory of diatomic and triatomic molecules meet an occasion to be applied in a broader, interdisciplinary context. Transferability of theory to larger, biologically important systems is the main idea for modelling quantum-mechanically relevant parts of the system and semi-classical treatment of the remainder of the system.

Another aspect relates to applications in everyday life. Having understood physical phenomena observed in certain systems, the next stage is a creative use of this knowledge, for example: more efficient methods for producing ultra-cold molecular ensembles, control of reactions which are of primary importance in industry or new implementations of medical therapies, such as the photodynamic therapy of cancer. Finally, the last but not least postulate of the present project is the predictive function of the developed theory, expecting to nurture tasks of creating new experimental challenges, henceforth prompting further progress in the field.

In a nutshell, **objectives of the present project are:**

- development of ro-vibronic quantum theory of polyatomic molecules in the presence intense electric and magnetic fields. Strong fields are capable of producing so called light-induced-potentials (LIP), which in turn can generate light-induced conical intersections (LICI) between electronic states of a molecule. A description of non-adiabatic nuclear dynamics near these light induced conical intersections is the prime theoretical objective. The theory is dedicated for implementation in a computer program, which propagate ro-vibronic wavefunctions in time for diatomic and triatomic molecules in arbitrary external fields.
- secondary objective is a theoretical procedure for assessing the influence of the geometric phase (Berry Phase) on non-adiabatic nuclear dynamics near the LICI, as well as, near the natural conical intersection. Is the geometric phase an artifact of the Born-Oppenheimer approximation? Does the geometric phase play a role in wavepacket dynamics at ultra-low temperatures, room temperature? Is there any theoretical evidence for the presence of this quantum-geometric property in the structure of bio-molecules and biological processes?
- the methodology and software developed as part of this project is designed to support detailed and accurate quantum-mechanical investigation of a variety of molecular processes, such as photo-induced chemical reactions (isomerisation, photo-dissociation, proton transfer, formation of weakly bound complexes), population control of molecular states (rapid-adiabatic-passage techniques), manipulation of externally coupled molecular degrees of freedom (cooling of molecules with dynamic Stark effect, alignment and orientation via THz pulses) or ultraviolet absorption spectra and photo-induced reaction pathways of atmospheric ozone, all with an unprecedented accuracy and spectral resolution. This will allow to elucidate and quantify subtle quantum effects, such as the geometric phase, often omitted in phenomenological models.
- the main applicative goal of the project is introduction of new concepts and techniques, dedicated for future experiments performed in collaboration with academic, industrial and medical laboratories. For example techniques of topological cooling of molecules in the optical Stark decelerator, alternative methods for enantiomer separation, manipulation of molecular geometry with light-induced-potentials, singlet-triplet conversion schemes, suppression or enhancement of photo-dissociation processes in biological and medical context, coherence control of vibrational wavepackets.

More detailed proposals for selected problems are given in section 4.

## 2 Motivation

This project has several sub-branches, which split into different disciplines. For this reason, motivation for each of the sub-branches is given separately, for the sake of transparency and accessibility. The scheme for the motivation section is as follows: ask what the problem is and what are the key issues? This is followed by a short resume on what has been done to solve this problem. Finally, propose how ideas presented below can contribute to the solution of the problem.

**Light-induced conical intersections and the geometric phase** Light-induced conical intersection (LICI) is a concept existing for almost two decades now [82]. A LICI appears when two electronic states intersect due to the presence of an external electric field and when the dipole coupling between the field and the molecule vanishes [18]. Rapid progress in the field was observed in the last few years. Papers by Corrales *et al.* [14], Kendrick *et al.* [36, 32], Halasz *et al.* [30], Chang *et al.* [11], Izmaylov *et al.* [33] and Sola [72] prove that the topic is in the highlight and becomes accessible with the state-of-the-art computational and experimental techniques. Theoretical and experimental studies of LICIs has almost entirely focused on simple diatomic systems [4, 72, 84].

In 2013 Demekhin and Cederbaum [18] presented a general theory of light-induced conical intersections in poly-atomic molecules in the Born-Oppenheimer approximation. This theory has not been yet applied to systems of practical importance. A very recent attempt by Sun *et al.* [1] has been made to simulate ro-vibrational wavepacket dynamics in the triatomic molecule ( $\text{H}_3^+$ ) under the influence of strong fields. However, the model presented by these authors, as operating in the Born-Oppenheimer and Condon approximations still possesses points for further improvement, which we believe, are able to provide. No non-adiabatic description of a triatomic system in vicinity of light-induced conical intersection has been given yet. At the same time, in a parallel and somewhat separate research channel, theoretical efforts have been made to answer the question about the geometric phase (GP) as whether or not being an artifact of the Born-Oppenheimer approximation [45]. Exact-factorization method introduced by Gross, Abedi *et al.* [21, 65, 74, 2] has been used to test this hypothesis on simple toy-models, which produce ambiguous answers so far. Geometric phase is believed to play role in suppression of vibrational wavepacket migration around conical intersections. Indeed, theoretical papers by Izmaylov *et al.* [33] suggest that the geometric phase, under certain circumstances, suppresses propagation of the vibrational wavepacket in vicinity of conical intersections. This phenomenon has a potential for numerous applications to molecular control. There has been two studies reported in this context on a polyatomic molecule by Kendrick *et al.* [36], and Althorpe *et al.* [34]; but only in the Born-Oppenheimer limit. Clearly, further investigation is here needed. Several questions related to the problems sketched above await answers: how do non-adiabatic effects manifest themselves in polyatomic molecules in strong electromagnetic fields? Are the natural conical-intersections (NCI) and light-induced conical intersections (LICI) identical in nature? Do topological effects influence nuclear dynamics around NCI and LICI? How can this knowledge be utilized in industry, medicine or astrophysics? To obtain reliable answers, and benefit from results, a more general theory is needed, able to replace existing models of the geometric phase and LICIs in a single study. This new methodology could be then tested on major atmospheric molecules, such as  $\text{SO}_2$ ,  $\text{CO}_2$  or  $\text{O}_3$ , giving insight into chemical processes in Earth's or exoplanet's atmospheres. Results of these tests should lead to proposals of new techniques for molecular control (cooling, bond-length control, control of molecular dissociation path, population transfer). Population transfer between electronic states, especially singlet-triplet conversion (ISC) is of primary importance in biological processes, such as conversion of triplet oxygen into singlet oxygen, release of singlet oxygen or hydroxyl radicals in photo-dynamic therapy of cancer, etc. [19, 46, 13].

The author is presently constructing a computer code for these purposes. As a basis for time-dependent ro-vibronic calculations two programs will be used: DUO by Yurchenko *et al.* [88] and DVR3D by Tennyson *et al.* [76]. DUO is a program for solving ro-vibronic Schrödinger equation for diatomic molecules and an arbitrary number of coupled electronic states, with spin-orbit coupling and other subtle effects. A number of recently published works establishes DUO as one of the best available options for high-accuracy computation of non-adiabatic nuclear dynamics in diatomics [43, 70, 55, 41, 57, 87, 75]. This code can be viewed as a beyond-the-Born-Oppenheimer version of the LEVEL program by R. Le Roy *et al.*. DVR3D suite [76] has capability of efficiently computing ro-vibrational wavefunctions, energy levels and transition dipole moments for triatomic systems using exact kinetic energy operator, a single potential energy surface and a single

dipole moment surface. Successful application of the DVR3D code to several atmospherically important molecules has been reported in the past [59, 61, 78, 89, 92, 91, 5, 79, 40, 62, 60]. Its multiple-PES version is currently tested on the  $\tilde{C}^1B_2$  state of  $\text{SO}_2$ , and comparative study to recent works by Field and co-workers [54] is planned. Having these powerful programs, it is straightforward to build time-dependent dynamics at unprecedented level of accuracy. To achieve this however, substantial computing resources may be required, which we believe modern high-computing-power clusters are able to provide.

**chemical reaction control** Control of chemical reactions of diatomic molecules with laser fields has been a goal pursued by several authors [63, 15, 27, 29, 35, 28, 58, 68] in the past decade. A number of studies targeted explanation of phenomena such as molecular geometry control [16, 38, 63] including bond softening and bond hardening in diatomic molecules, laser adiabatic manipulation of the bond (LAMB) scheme [10], control of lifetimes of states [72], control of quantum yield (e.g. photo-isomerisation yields), or for example suppression of migration of vibrational wavepacket through quantum interferences near LICIs [48]. Many of these phenomena were interpreted in terms of light-induced potentials. There are still open challenges in the field of control of diatomic molecules, as pointed in recent review on strong laser chemistry by Sola *et al.* [72].

For example, the role of the geometric phase near LICIs [30] has been only partially clarified in a case study on a model system. For this reason, an extensive and high level of theory treatment with inclusion of non-adiabatic effects is needed. Signatures of experimental control of chemical reactions with laser light in complex molecules has been recently presented in the work by Meyer *et al.* [44]. An exciting theoretical avenue could be opened, by continuing on this study. For instance, non-resonant dynamic Stark effect (NRDSE) scheme of Sussman, Stolow and coworkers [73] can be used in manipulation of dissociation rates, by changing local shape of the PES. Only few simple systems has been investigated in this context so far. Also, techniques of alignment and orientation of diatomics with THz pulses, are presently at the frontier. Bisgaard *et al.* [9] has empirically shown a possibility for spectroscopic probing of the molecular quantum states for an aligned in space  $\text{CS}_2$  molecule, thus further exploration of various techniques of control of rotational motion of molecules appears particularly interesting. Another motivation point comes from pharmaceutical industry and chemistry of life, where differentiation and separation of enantiomers play central role. Tailored, multi-color electromagnetic fields have been found to allow for efficient enantiomer differentiation, by measuring differences in phase of the emitted radiation by the two enantiomers [83, 56]. In polyatomics, a recent theoretical study has been reported on weakly bound  $\text{H}_2\text{He}^+$  complex Szidarovszky2016. The  $\text{H}_2\text{He}^+$  example is presented as potentially applicable in interpretation of processes of molecular formation in the interstellar medium. Also, it has been noted that photo-dissociation dynamics is severely changed by the weak He perturber. This, in author's opinion may have far reaching consequences and applications, for (a naive) example, modification of hydrogen bond strength in DNA molecules, by saturation with inert gas. Experimental work by Corrales *et al.* [14] on laser control of dissociation in  $\text{CH}_3\text{I}$  indicates a rapid progress in the field toward larger systems. Photo-isomerisation of 3-cyclohexadiene [37] by T. Martinez group or photo-dissociation of  $\text{NH}_3$  with non-resonant bond-length control [66] by Richings and Worth prove that molecules with many atoms, perhaps even bio-molecules, are within reach of available methods. These tasks often require accurate wavefunctions for ro-vibrational states up to dissociation, which represents another grand challenge in modern nuclear motion theory.

Revision of literature in this broad field leads to the conclusion, that advanced tools used in nuclear motion theory of diatomic and polyatomic molecules, which serve at highest currently possible level of theory, can be readily utilized to open exciting perspectives for applications of light-induced phenomena in various devices or branches of science.

An interesting perspective in nuclear dynamics influenced by strong external fields is theoretical prediction and experimental quantification of effects (e.g. wavepacket interference, molecular dissociation, geometric distortions) and mechanisms (e.g. population transfer [24], cooling), which are subtle enough to fall under the uncertainty introduced by the BO approximation, and neglecting the GP.

**Quantum population transfer** Rapid-adiabatic-passage (RAP) techniques have become very successful in the last decade. Experimental and theoretical studies have been dedicated to development of efficient, selective, and robust procedures for preparation of atoms and di-atomic molecules in a target quantum state. Techniques such as Stark-chirped rapid adiabatic passage (SCRAP) [85, 67, 64], Stimulated-Raman

adiabatic passage (STIRAP) [8] presently allow for almost 100% controlled population transfer between quantum states of atoms [85, 39], and more recently ro-vibrational and ro-vibronic states di-atomic molecules [51, 50, 47, 81, 20, 26]. An implementation of SCRAP in universal quantum gates in quantum computers has been recently suggested [49, 12, 71]. However, only a small number of theoretical studies has been published on the possibility of application of these successful methods to polyatomic molecules. These works, although pioneering, often incorporate simplistic models with normal vibrations and model-toy potentials, what is convenient for introduction of the idea and its intuitive understanding. However no study, except very recent publication by Zak and Yachmenev [90] on the ammonia molecule, provide a comprehensive and high-accuracy theoretical treatment of rapid-adiabatic-passage in polyatomic molecular systems. Only a simulation of a system existing in nature, with a perspective of industrial or medical application, gives a chance to yield a seminal work, which can be continued in the laboratory.

Another important, yet largely unexplored aspect of the control of quantum states is a possibility of utilizing RAP techniques in population transfer between light-induced potential surfaces in so called adiabatic passage by light-induced potential (APLIP) technique [24, 25, 68, 26]. This problem appears particularly exciting, as it combines separate branches of molecular physics: nuclear motion theory in used molecular spectroscopy and coherent control of quantum states extensively developed in the area of quantum optics; with prospective applications possible in yet another sub-branch of chemical physics: chemical reaction control. The idea of APLIP still awaits a general theoretical description at rotational-vibrational-electronic level in the non-adiabatic regime; also a publicly available and widely recognized computer software for APLIP simulation purposes is needed. APLIP and its modified versions could be used, for example, in simulations of electronic singlet-triplet conversion in the oxygen molecule, which is the key compound in photo-dynamic therapy of cancer. Singlet oxygen is usually released by photo-dissociation from a bigger photo-sensitizer molecule. Thus, O<sub>2</sub> bonded to a transition metal, as in heme molecule, can be considered as a triatomic part of a bigger system [18, 69]. Then, very accurate quantum predictions become possible even for biological molecules, such as heme [23]. The reminder of the molecule is treated semi-classically [69, 3, 23] with little loss in accuracy. For this reason, several other biologically significant applications, such as hydrogen bond breaking via population transfer to dissociative states or selective excitations in DNA, could become a viable research path for future years. To the best of author's knowledge no study has assessed the role of the geometric phase in RAP processes for electronic transitions in vicinity of conical intersections and no high-accuracy methodology or software has been used to study coherent control of ro-vibronic populations of states in polyatomic molecules in a beyond the Born-Oppenheimer framework.

**Ultra-cold molecules and chemistry** Recently we have proposed a method of controlling population of ro-vibrational states of molecules in the Stark decelerator [90]. Two color chirped-pulses enabled more efficient and phase-space stable slowing of molecules inside the Stark decelerator. A continuation of this work in the context of light-induced dynamics could introduce further improvements to cooling techniques, aiming in setting a new standard for generation of ultra-cold molecules. This field is dynamically developing. Currently the most popular methods for generating ultra-cold molecules are: microwave cavity cooling, Stark or Zeeman deceleration, sisyphus cooling, or deceleration on a chip. There are however several issues one has to face when attempting to slow polar molecules to sub-Kelvin temperatures. Often, accurate models for intra-molecular ro-vibrational relaxation are needed for explanation of results of experiments. Input data (energy levels, transition probabilities) for such models can be taken from highly accurate ro-vibrational calculations, already stored in a form of publicly available database, as suggested in our recent paper [52]. Having in hand tools needed for quantitative explanation of experiments, proposition of new techniques is the next step to follow.

**Machine learning in molecular physics** Neural networks give an exclusive opportunity to generate high quality potential energy surfaces for systems with many degrees of freedom [6, 42, 86, 7]. Surfaces used in the present project could be prepared using neural network fitting technique [42]. Machine learning techniques, although gradually more popular, still appear to be largely unexplored and sometimes underestimated in molecular science. The present project is a response to this niche. Neural networks could be used as an advanced tool in optimal control of molecular states, pattern recognition purposes or prediction of molecular properties.

**Light-induced Pseudo-Jahn-Teller effect** Observation of signatures of the geometric phase, through half-integer quantization of the pseudorotational motion in  $\text{Na}_3$  molecule, has been reported three decades ago [17], prompting a long and dynamic debate [22, 65, 80] on the influence of the geometric phase effect on molecular energy levels and dynamics. Surprisingly, only few accurate theoretical studies have been dedicated to provide comprehensive explanation of this phenomenon (see for example ref.[31]).

An interesting case study for methodology developed in this project would be therefore Jahn-Teller or Pseudo-Jahn-Teller molecules in strong laser fields, where light-induced potentials are generated. Population transfer, laser induced tunnelling splitting or cooling via hindered pseudo-rotational motion of nuclei, are only few examples of exciting phenomena to be studied. Ultimate answer to the question about fractional quantization of pseudo-rotational motion of nuclei in sodium trimer  $\text{Na}_3$  is another challenge [17, 22, 65, 80]. Several attempts have been made to give reliable answer to this question; recently on a model system using exact-factorization method. Can external fields generate potentials that would lower the symmetry of the molecule and create 'light-induced Jahn-Teller effect'? This problem could be later generalized to larger molecules, as done in ref. [77]. DVR3D software, when adjusted to multiple electronic excited states, should be capable of giving precise insight into the problem of the Jahn-Teller effect, pseudo-rotational motion and their relation with the geometric phase in the presence of external fields. Short-lived modulation of diagonal and transition dipole moments in a diatomic molecule, introducing perpendicular components of the body-fixed dipole moment may lead to normally forbidden electronic transitions. Such short-lived weakly bounded complexes could find medical applications, through modification of biological reaction paths by inert gas, e.g. infra-red or Raman activation of selected hydrogen bonds.

### 3 Methodology

Stationary Schrödinger equation for diatomic molecules is be solved using DUO suite [88]. This code has capability of calculating ro-vibronic wavefunctions, energy levels and transition intensities for diatomic systems with arbitrary number of coupled potential energy surfaces. A number of published recent works establishes DUO as one of the best available options for high-accuracy treatment of non-adiabatic nuclear dynamics in diatomics. Astrophysical and atmospheric science applications of the DUO procedure have been a subject of recent publications [43, 70, 55, 41, 57, 87, 75].

DVR3D suite [76] is be used to compute ro-vibrational wavefunctions, energy levels and transition dipole moments for triatomic systems. Successful application of the DVR3D code to several atmospherically important molecules has been reported in the past [59, 61, 78, 89, 92, 91, 5, 79, 40, 62, 60].

A theoretical model of vibronic coupling in the presence of external fields is expected to be developed, implemented and solved for stationary states of triatomic molecules. Diabatisation scheme will be partially based on the work by Koppel *et al.* [53], and partially on the currently developed by the author *quasi-hermitian representation method*, which borrows techniques from Quantum Field Theory. Such approach generates links between sub-disciplines of Physics and synthetically transfers techniques to molecular physics. A separate Fortran code for time-dependent propagation of the ro-vibronic wavefunction will be written. Split-operator method with Chebyshev expansion will be used. Initial wavefunctions will be taken from DUO or DVR3D; geometric phase will be included in the calculation. Results for  $J = 0$  will be compared to MCTDH calculations, providing a benchmark study.

## 4 Proposed research sub-topics

This section contains proposals of specific research topics, and is a logical continuation of *motivation* section. Ideas sketched below should be viewed as a preliminary and general research plan and are subject to adjustments. Which topic to choose in the first instance is a subject for discussion with the host institution and funding bodies. The author is also opened to suggestions from group members of the host institution; changes, adjustments, and research topics from outside the list below are totally possible.

### 4.1 Topologically controlled dissociation of diatomic molecules

In diatomic molecules, light-induced conical intersections (LICIs) can only be created if two conditions are satisfied simultaneously: energetic match between two electronic states and vanishing dipole coupling [18]. The former condition can be satisfied by properly tuning incident laser frequency and the latter condition is satisfied by aligning the molecule perpendicularly to the incident electric field [30, 48]. For a molecule with electronic structure similar to  $\text{H}_2^+$ , one can think of generation of a gaussian ro-vibrational wavepacket in the electronic excited dissociative state with an intense laser pulse. The wavepacket is created in the Franck-Condon region and shortly after begins to move along the upper unbound potential energy curve toward dissociation. However, if on the same time-scale another LICIs is produced on the path of the wavepacket, then the wavepacket is given a chance to hop between surfaces and return to its electronic ground state, what prevents dissociation. Location and geometry in vicinity of LICIs can be controlled with frequency and intensity of the laser pulse. Such situation can only occur when the molecule is aligned perpendicular to the external field. Alignment of molecules can be efficiently achieved for example by using a train of picosecond THz pulses [52]. Spectroscopy of aligned in space molecules has been demonstrated experimentally by Bisgaard *et al.* [9] on the example of  $\text{CS}_2$  molecule. For these reasons, an experiment where a THz-induced-alignment and suppression of dissociation takes place should be possible. Also, reverse situation may be possible: for a particular alignment, enhancement of dissociation can be triggered by the LICIs. In both cases the cross section for dissociation should strongly depend on the angle between molecular long axis and Z-axis of the LAB frame. Theoretical description of this problem would involve computation of ro-vibronic stationary states of a diatomic molecule and simulations of wavepacket dynamics with time-dependent external fields; all done using the developed methodology and software.

### 4.2 Alignment through bound states of Light Induced Potentials

Molecules in a field-free environment rotate freely in space. Only very intense laser fields are capable of providing some level of alignment or orientation. When an external electric field is switched on, the angle orienting the molecule with respect to the LAB frame serves as a dynamical variable. Therefore, for a diatomic molecule it is possible to generate two dimensional potential energy surfaces by applying appropriate external fields. For example, sodium dimer  $\text{Na}_2$  has been found to possess 'bound' light-induced electronic ground state [30]. Light induced PES (LIPES) of the first singlet electronic excited state represents a bound state with conical intersection at 90 degree alignment with respect to the external field. For this reason, one can think of an experiment where a pump laser transfers adiabatically the molecular population into the first singlet electronic excited state and at the same time, another pulse generates LICIs, adding another degree of freedom to the potential energy of the system (field+molecule). In such generated 2D bound PES, the wavepacket migrates along the steepest energy descent path, hence toward the conical intersection and the perpendicular alignment. Because the 2D LIPES of the electronic ground state depends on a periodic coordinate and at the same time this PES is not completely flat in this coordinate, some alignment angles will be favoured over others. In the case study by Halasz *et al.* [30] the global minimum of the ground state LIPES locates the  $\text{Na}_2$  molecule parallel to the external field, as expected. If the frequency of the external laser is slightly detuned from resonance, the LICIs at perpendicular orientation will vanish and hopping between surfaces will be suppressed. This should give a possibility of choice of alignment (parallel or perpendicular) by moving populations between the electronic states. Orientation could be also achieved by breaking the angular symmetry of LIP. This could be done by spatially non-uniform external field, which would prefer certain orientations. (Please note that listed above are only tentative suggestions for a closer investigation).

### 4.3 Differentiation of chiral compounds using quantum interference

This problem, in principle, appears similar to the alignment through bound states of LIPs. Differentiation of chiral molecules has been shown to be possible by employing linearly polarized intense ultra-short laser pulses with skewed mutual polarization [83]. This method is an alternative to the three-wave mixing technique also used in enantiomer differentiation [56]. Present idea is not yet well developed, and relies on suggestion that off-diagonal molecular polarisabilities can interact with external electric field and cause little distortions to the LIPES. Then, vibrational wavepacket created by appropriate laser fields evolve to produce different interference patterns around CIs or LICIs, so that the wavepacket ends up in different states depending on the absolute configuration of the species (i.e. wavepackets of two different enantiomers evolve toward different final states). Emission from these final states should give quantitative, spectroscopically available measure of the enantiomeric excess.

### 4.4 Stabilization of a wavepacket via light-induced conical intersections

The position of LICIs can be controlled by manipulating the frequency of the laser field. At the same time, steepness and local shape of the LIPES can be modified by changing the intensity of the laser field. These two effects leave space for manipulation of ro-vibronic states. As an example, one can think of generating a highly excited Gaussian wavepacket in the electronic ground state and generate a pilot LICl with one of the electronic excited states to suppress migration of the ro-vibrational wavepacket down along the ground state PES. This suppression is caused by the geometric phase effects, which lead to destructive interference of the wavepacket when encircling the CI from two opposite sides [36, 33]. In general, more than one LICl can be generated, producing a complex topological arrangement, which could open a number of possibilities for control of motion of the ro-vibrational wavepacket. Such study in the context of the geometric phase creates an opportunity for discovering bits of new physics.

### 4.5 Light-induced Pseudo-Jahn-Teller effect

To the best of author's knowledge, LIPs for triatomic molecules have not been studied experimentally or theoretically yet. Works by Garraway *et al.* [24], Arasaki *et al.* [4], Corrales *et al.* [14], Kendrick *et al.* [36, 32], Halasz *et al.* [30], Chang *et al.* [11] and Izmaylov *et al.* [33] focus on diatomic molecules with two intersecting LIPESs. For this reason, a theoretical study on diatomics with more than two electronic states involved in light induced dynamics would be of primary interest. At the same time, a triatomic system with the Pseudo-Jahn-Teller vibronic interaction (e.g. sodium trimer Na<sub>3</sub>, or very recent suggestion of the C<sup>1</sup>B<sub>2</sub> state of SO<sub>2</sub> [54]) could serve as a model for application of the general theory introduced by Demekhin *et al.* [18] to polyatomics. The author recently calculated a high-quality PES for the C<sup>1</sup>B<sub>2</sub> state of SO<sub>2</sub>. For reasons presented above, a full ro-vibronic model will be proposed on the basis of the existing ro-vibrational code DVR3D [76]. A new method of 'quasi-diatization' proposed by the author will be employed. This method borrows techniques known in quantum field theory for many-body interactions, and although inherently approximate, has a chance to be robust and easy to implement. As a starting point, diabatization scheme by Pacher, Cederbaum and Koppel will be considered [53]. Having a vibronic model for regions near intersecting surfaces, the plan is to investigate bound states and wavepacket propagation built on these bound states for a triatomic system exhibiting the Pseudo-Jahn-Teller effect. External laser field will be responsible for generation of light induced conical intersections of dimensionality 2. Both 'mechanical' and 'dynamical' non-adiabatic effects will be discussed - this has not been done before. There is an important question to answer about mutual influence of neighbouring conical intersection on the wavepacket dynamics. How does the geometric phase manifest itself in such a model? Is the geometric phase an artifact of the Born-Oppenheimer approximation [45]?

### 4.6 Topological cooling: optical Stark decelerator

Recently we have proposed a method for controlling population of ro-vibrational states in the Stark decelerator [90]. Here, a similar concept, but utilizing laser fields alone, is proposed. Consider a cavity with a standing wave with high electric field intensity. The intensity of the field is high enough to put molecule into a dressed-state, i.e. generate the light-induced potential. LICl appears when two electronic states intersect

due to the presence of external electric field and dipole coupling between the field and the molecule vanishes [18]. The latter condition can be satisfied by aligning molecule perpendicular to the incident electric field [30]. Assume a beam of polyatomic molecules entering the cavity with a standing wave. Then the centre-of-mass motion of the molecule becomes coupled to the electric field. Periodic changes in the field will be experienced by the molecule along propagation path. Hence, the criterion for matching energies of dressed-potential energy surfaces can be fulfilled only at points with the same value of the electric field. There are two such points in a single unit cell in the cavity: one located in front of the peak of the standing wave and the other located symmetrically behind the peak intensity. If the molecule is properly aligned a LICI will appear at these points. The generated LICI will be positioned at a fixed point on the LIPES, hence should affect only selected vibrational levels of the molecule for the ground and electronic excited state. In other words, the field from the standing wave can serve as a source of the Stark shift of ro-vibrational energy levels (because the LIPES is not only shifted with respect to the zero-field surface, but also slightly distorted, due to interaction of the molecular polarisability and the dipole moment with the electric field)[4]. When the molecule arrives in the LICI point, another laser, called the pump laser will be switched on to allow for population transfer between low-field-seeking and high-field-seeking states. This population control will allow for efficient slowing of the centre of mass of the molecule with the field in the cavity. The force exerted on the molecule is  $\vec{F} = -\nabla W(E)$ , where  $W$  is the Stark shift induced by electric field of strength  $E$ . The higher the population of appropriate states is, the more efficient the cooling will be. The LFS-HFS transition must involve long-lived states, for example low  $J$  inversion states of ammonia or states belonging to low  $J$ s (or a ro-vibrational wavepacket with different  $J$ 's and vibrational quantum numbers) of a singlet and a triplet electronic state. The only requirement is that overall energy of the superposed state (wavepacket) is dissipated (in the HFS state) or absorbed (in the LFS state). This wavepacket can be then forced to migrate between potential energy surfaces through the LICI. The role of the pump pulse is to increase the *Rabi frequency* and enable adiabatic population transfer. Similar field-chirped technique has been proven to be a stable way of transferring quantum populations between selected states with very high efficiencies [51, 85, 20, 72, 64, 24]. This hypothetical modification of Stark-chirped rapid adiabatic passage (SCRAP) technique could be called light-chirped rapid adiabatic passage (LCRAP). LCRAP could be used, for example, in singlet-triplet conversion in oxygen molecule, which is the essential compound in the photo-dynamic therapy of cancer. Several other bio-important applications, such as hydrogen bond breaking or selective excitations in DNA could become a prospective application of methods discussed above [3, 23]. Also a part of a bigger system can be treated as a triatomic molecule [18, 69]. Then very accurate quantum predictions become possible even for biological molecules, such as Heme [23]. The reminder of the molecule can be treated semi-classically [69].

#### 4.7 Tunnelling splitting in light-induced potentials; laser induced vibrational relaxation

Light-induced potential generated in a Jahn-Teller molecule (e.g.  $\text{Na}_3$ ) can couple two zero-field PESs, generating an intersection of the *mexican hat* potential with the PES of a higher excited electronic state. Assume that the pseudo-rotational motion of atoms is not significantly hindered by the presence of the intersection [17, 80] (as in  $\text{Na}_3$ ). In such situation however, the full  $2\pi$  rotation in the pseudo-rotational coordinate will cause that two conical intersections are encircled: one located in the centre of the frame of reference and the other, also rotationally symmetric, resulting from the action of the external field. Investigation of the behaviour of the geometric phase in such system is a really interesting challenge. Vibronic interactions could prohibit creation of the LICI, hence such system appears to be a good candidate to answer the question about the geometric phase being an artifact of the Born-Oppenheimer approximation [45]. Another idea to explore comes with generation of a double-well structure resulting from intersecting surfaces. Tunnelling splitting of stationary states of such field-dressed system is hypothetically possible. A possibility of cooling of internal molecular degrees of freedom by the Sisyphus type mechanism could be also considered (the well known problem of preparation of molecules in the quantum ground state).

## 4.8 Quantum dynamics for therapies of cancer

Porphyrin based molecules are widely used as photo-sensitizers in the photo-dynamic therapy of cancer [13, 19, 46]. It is important to understand the dynamics of photo-dissociation of active species in such molecules, which can be achieved by time-dependent ro-vibrational simulations. Similarly, larger systems such as oxyhemoglobin, methemoglobin or hydrogen-bonds in DNA molecules can be considered. These biologically important molecules usually possess few-atom active centres, which are interesting from the chemical point of view. Therefore a mixed quantum-classical computation is planned to provide a high quality description of the active centre (e.g. Fe-O<sub>2</sub>) within the developed methodology, and treatment of the remainder of the system as an averaged external field.

## 4.9 Prospective collaborations

- Theory/Experiment: R.W. Field *et al.*: Department of Chemistry, MIT, Cambridge MA, USA.
- Experiment/Theory: L. Banares, I.R. Sola *et al.*: Department of Physics, CSIC, Madrid, Spain.
- Experiment/Theory: J. Kuepper, A. Yachmenev *et al.*: Center for Free-Electron Laser Science (CFEL), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany.
- Experiment: M. Tarbutt *et al.* - Department of Physics, Imperial College London, London, UK
- Theory: B. Kendrick - Los Alamos National Laboratory, New Mexico, USA
- Theory: S. Althrope - Department of Chemistry, University of Cambridge, Cambridge, UK.
- Theory: J. Richardson *et al.* - Department of Chemistry and Applied Biosciences, ETH, Zürich, Switzerland.

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