Self-presentation

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- 2002 r.: Uniwersytet Warszawski, Wydział Chemii, MSc degree; title of thesis: *Dispersion energy in the open-shell Van der Waals systems in the random phase approximation.*; supervisor - prof. Robert Moszyński;
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4 The scientific achievement:

(a) Title of the scientific achievement
Series of publications:
„Interactions and collisons of ultracold atoms and molecules."

(b) authors, titles, year of publication, name of the journal:
more detailed contributions are given in separate Appendices, including statements of the other coauthors.

[H1] Piotr S. Żuchowski, Jeremy M. Hutson
„Reactions of ultracold alkali-metal dimers"
Phys. Rev A 81, 060703 (2010)
citations: 66
my contribution to the paper: 75%

[H2] Piotr S. Żuchowski, Maciej Kosicki, Monika Kodrycka, Pavel Soldan
„van der Waals coefficients for systems with ultracold polar alkali-metal molecules"
Phys. Rev. A 87, 022706 (2013)
citations: 1
my contribution to the paper: 30%

[H3] Piotr S. Żuchowski, Jesus Aldegunde, Jeremy M. Hutson
„Ultracold RbSr molecules can be formed by magnetoassociation"
Phys. Rev. Lett. 105, 153201 (2010)
citations: 31 my contribution to the paper: 60%

[H4] Piotr S. Żuchowski, Jeremy M. Hutson
„Prospects for producing ultracold NH_3 molecules by sympathetic cooling: A survey of interaction potentials"
Phys. Rev. A 78, 022701 (2008)
citations: 20
my contribution to the paper: 70%

[H5] Pavel Soldan, Piotr S. Żuchowski, Jeremy M. Hutson
„Prospects for sympathetic cooling of polar molecules: NH with alkali-metal and alkaline-earth atoms – a new hope"
Faraday Discussions 142, 191 (2009)
citations: 25
my contribution to the paper: 40%

[H6] Piotr S. Żuchowski, Jeremy M. Hutson
„Low-energy collisions of NH_3 and ND_3 with ultracold Rb atoms"
Phys. Rev. A 79, 062708 (2009)
citations: 33
my contribution to the paper: 80%

[H7] Piotr S. Żuchowski, Jeremy M. Hutson
„Cold collisions of $N(^4S)$ atoms and NH ($^3\Sigma^-$) molecules in magnetic fields"
Phys. Chem. Chem. Phys. 13, 3669 (2011)
citations: 16
my contribution to the paper: 75%

[H8] Michał Hapka, Grzegorz Chałasiński, Jacek Kłos, Piotr Żuchowski
„First-principle interaction potentials for metastable He(^3S) and Ne(^3P) with closed-shell molecules: Application to Penning-ionizing systems"
J. Chem. Phys. 139, 014307 (2013)
citations: 1
my contribution to the paper: 40%

(c) discussion of the scientific goals, results obtained, and their applications:

4.1 Introduction and motivation of research.

Since rapid development of laser techniques in 70. one of the most intensively explored area of current atomic and molecular physics is control of the matter with electromagnetic fields. In particular, one of the most challenging topic in the field was cooling the atoms to the nanokelvin regime, where they can form new state of matter. In the 80. the laser cooling and trapping techniques emerged, mostly due to the contribution of groups led by Claude Cohen-Tannoudji, William Phillips and Steven Chu [1–3]. These three scientists have been awarded Nobel Prize in Physics in 1997 for development of laser cooling and trapping techniques. In the year of 1994 another groundbreaking achievement in cold matter physics has been reported: the groups of Eric Cornell and Carl Wiemann, and the group of Wolfgang Ketterle [4, 5] produced the Bose Einstein condensate of alkali atoms, which was also awarded with Nobel Prize in Physics, in 2002.

During the second half of 1990. the ultracold matter physics started to develop rapidly in many laboratories over the world, as the community realised the great potential hidden in exploring the quantum gases. Soon afterwards, many interesting proposals for the applications of cold molecules were reported. These applications might revolutionise many areas of physics: quantum information theory, many-body physics, condensed matter physics, metrology, high-precision spectroscopy or chemical physics. Few years after successful production of quantum-degenerate gases the ultracold physics community turned to more complex systems which can be produced from atoms – to cold molecules. Molecules exhibit much more complex internal structure than atoms: they have vibrational, rotational and hyperfine energy levels, and they also interact strongly with electric field. An interesting feature of molecules, very distinct from atoms is the character of interactions they experience. Polar molecules experience huge anisotropy of the interaction and the interaction itself has much more attractive behaviour than atoms (R^{-3} in case of polar molecules, R^{-6} in case of atoms).

As an example application of ultracold, polar molecules in quantum information theory one can mention the proposal published by DeMille [6]: it was suggested, that the molecules confined in optical lattice and interacting with electric field can act as q-bits and serve as

a prototype quantum computer. The group of Zoller proposed [7, 8] to use cold, polar and paramagnetic molecules as a constituent of quantum simulator to study the phase transitions in condensed matter. A great deal of applications of cold molecules involves high-precision spectroscopy for the tests of fundamental theories in physics. For example, spectroscopy of YbF molecules was proposed to measure the electric dipole moment of electron [9], while the transitions in OH molecules were used to test time-drift of fine structure constant [10].

Since the very beginning of studies on cold molecules, two classes of methods were established, as a possible ways to produce cold samples of molecules: 1) direct methods - based on idea of cooling stable molecules from high to low temperatures using the combination of fields, or thermalization with colder gases; 2) indirect methods, which rely on association of pre-cooled ultracold atoms using photons or magnetic field. The first class of methods still are not able to cool the molecules to microkelvins nevertheless, several interesting experiments toward the production of microkelvin cold molecules have been reported, for example evaporative cooling of OH molecules, or attempts of sympathetic cooling of deuterated ammonia by Rb atoms [11]. Variety of energy levels of molecules is at the same time, a nightmare for laser cooling, since it is very hard to find an appropriate closed laser cooling transition (except very narrow class of molecules). The second approach was very successful: in 2008 ultracold samples of KRb, Cs_2 and LiCs molecules have been produced via magnetoassociation followed by stimulated Raman adiabatic passage (STIRAP) or photoassociation followed by spontaneous decay [12–14].

The goal of this series of the publications is to answer the most important questions posed by leading experimental groups in the field:

- is it possible to produce a stable ultracold gas of alkali-metal dimers?
- is it possible to produce weakly bound molecules of atoms with different spins?
- what is the nature of ultracold atom+molecule collisions?

The first of these questions was posed following the successful production of KRb and LiCs molecules. A necessary condition for molecular Bose-Einstein condensate is that the appropriate molecules are collisionally stable. If these molecules are in their absolute ground state, the only inelastic process which might occur is the chemical reaction: atom exchange or trimer formation. Here we present papers **[H1,H2]** devoted to studies of the interactions in the systems AB+AB and AB+A, where A and B are alkali metal atoms. In these papers we evaluate the energy differences for the chemical reactions, which might occur in quantum gases of AB molecules. We also calculate relevant van der Waals C_6 coefficients, which govern the interactions of AB molecules at long range. We provide the detailed description of this problem in Section 4.2.

A motivation to study the association of atoms with different electronic spins is the production of paramagnetic, polar molecules. These molecules might have a big potential, since they could be manipulated with a combinations of magnetic and electric fields. Such molecules have been proposed by Zoller group as constituent of quantum simulators of many-body Hamiltonians (such as Hubbard Hamiltonian) to study the phase-transitions in a bulk matter [7]. To associate the atoms into weakly bound molecules the Feshbach resonances are essential. To date, the mechanisms which drive the Feshbach resonances for alkali-metal dimers are well-known and magnetoassociation, and Feshbach manipulation of alkali-metal atom is well established technique. The mechanisms of magnetic Feshbach resonances in mixed systems of different spins, such as Rb+Sr were completely unknown prior the publication **[H3]**. We present here the discussion of the paper **[H3]** where we demonstrate the entirely new mechanism which drives Feshbach resonances, which could be used to magnetoassociation of molecules or controlling their interaction in the ultracold gas. The discussion of this paper is given in the Section 4.3.

Third problem included in the selection of publications, which will be given in Section 4.4, are the interactions and collisions of molecules (H_2, ammonia, NH) with atoms, which could be obtained in temperatures on the order of mK (metastable helium, denoted as He*, N) or μK (Rb, other alkali-metal atoms, alkaline-earth atoms). This research was inspired by new experiments [15,16] on collisions of velocity-controlled atomic and molecular beams, molecular trapping of directly cooled molecules, and sympathetic cooling. Theoretical description of such collisions involves solving several problems: first, potential energy surfaces need to be evaluated using quantum chemistry methods, secondly, Schroedinger equations for nuclear motion need to be solved. The papers **[H4, H5]** are focused on the first-principles calculations of interaction potentials for the systems consisting of 1st and 2nd group atoms with ammonia, and NH molecules. The paper **[H6]** contains the study of Rb+NH_3/ND_3 collision dynamics based on potential energy surface developed in the paper **[H4]**. In this paper broad range of collision energies is investigated (from microkelvins to hundred of kelvins) and we are trying to address several important issues: the origin and density of resonances, ratio of elastic to inelastic collision cross-sections, sensitivity of calculated collision cross-sections to *ab-initio* potential energy surfaces. The paper **[H7]** from the series of publications contains the study of potential energy surface and collision dynamics of N+NH system in the magnetic field to study the spin-changing collisions (Zeeman relaxation), crucial in sympathetic cooling of atoms by paramagnetic molecules. Finally the publication **[H8]** challenges the most recent experimental studies of low-energy collisions of He*+H_2 i He*+Ar [17]. In the paper **[H8]** we investigate the potential energy surfaces in these systems and provide the *ab initio* predictions of the positions of shape resonances in He*+H_2 i He*+Ar. In fact all the works **[H4–H8]** can be regarded

as a test of quantum chemistry in calculating potential energy surfaces, and predicting the collisional properties.

The Section 4.5 summarizes the series of publications and discusses its impact on the field.

4.2 Chemical reactions and interactions of ultracold alkali-metal dimers

Indirect methods of production of cold molecules has been implemented more than 10 years ago. The first success of these methods was photoassociation of the cesium atoms to the electronically excited molecules [18]. These molecules however, have extremely short lifetime, due to their spontaneous emission and collisional instability. Shortly afterward the techniques of association of atoms into molecules with time-dependent magnetic fields (magnetoassociation) were developed [19]. A real breakthrough in cold matter physics was the production of ground state molecules, from the weakly-bound molecules by STIRAP. In this manner, group of Jin and Ye (from JILA, Boulder, US) produced KRb molecules [12].

The molecular Bose-Einstein condensates can be produced only if the constituent molecules do not react among themselves when they are brought to the contact. The processes that potentially might occur are

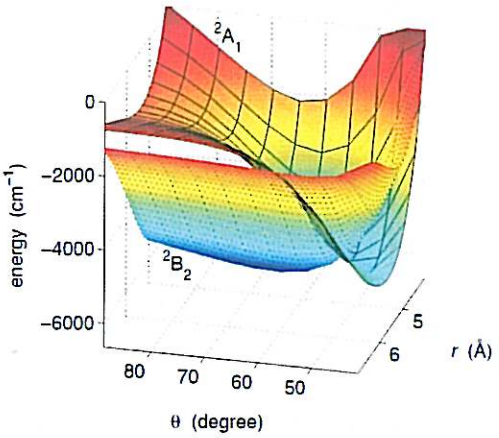
i) $AB+AB \rightarrow A_2 + B_2$

ii) $AB+AB \rightarrow A_2B+B$

when A and B are alkali-metal dimers. To guide the experimentalist which molecules are the best for production of molecular condensates we have to explore these two reactions. The publication **[H1]** investigates the energy differences in above chemical reactions for all possible alkali-metal dimers. As a matter of fact, for the first chemical reaction the *ab initio* studies are not necessary at all, but we only have to compile the existing spectroscopic data of binding energies for appropriate alkali-metal dimers. It turns out that all dimers containing Li atom as well as KRb are subject to chemical reaction of type i) and the energy release in the reaction is far too large to keep them in the optical trap after the reaction. It is much more difficult to study the second possibility - the trimer formation. To this end, state-of-the-art *ab initio* calculations with quantum chemistry methods are essential and the crucial issue is to find the minimum energy for AB_2 system in the doublet state. In paper **[H1]** we have used averaged-quadratic coupled-clusters method (AQCC) introduced by Lischka and coworkers [20]. We have also used the large effective core potentials with core polarization potentials (ECP+CPP) to describe inner electrons of alkali atoms [21]: they include all electrons except the last, valence electron.

To better understand the electronic structure of dublet states of alkali trimers let us first consider the homonuclear trimers. In equilateral triangle geometry D_{3h} molecular orbitals

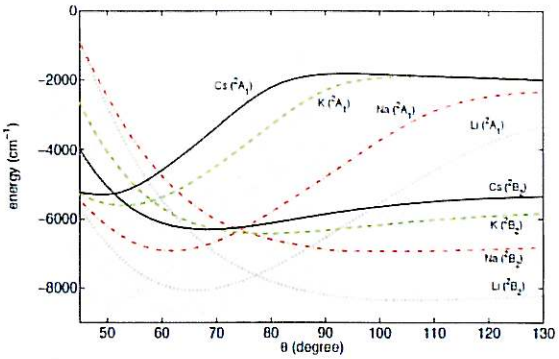
Rysunek 1: Potential energy surfaces of the $^2B_2$ and $^2A_1$ states in the Rb_2Cs system in C_{2v} geometry, as a function of RbCs bond length and angle. The crossing of these states occur for the angles close to 50°.



which originate from atomic s orbitals have symmetry a_1 and e, hence the electronic configuration of the system is $a_1^2e^1$ and the system has symmetry ^2E. This state is subject to Jahn-Teller distortion to the geometry C_{2v}. In C_{2v} the orbital of symmetry e is reduced to a_1 and b_2 symmetries. All homonuclear systems have equilibrium geometry of C_{2v} symmetry and the calculations demonstrated that they have $^2B_2$ symmetry.

In the systems AB_2 the point group of highest symmetry is C_{2v}, for which the AB_2 can be either in $^2B_2$ or $^2A_1$ symmetry. In the Figure (4.2) we show the surface plot of those states for Rb_2Cs. We can see, that for the angle of 50 degrees the surfaces intersect. The intersection is only for C_{2v} geometry, but it is also possible that system undergoes further distortion to C_s geometry. A good illustration of behaviour of interaction energy of trimer (in fact: the atomization energy) is also the Figure (4.2), where we present the minimum energy for fixed angle between bonds. In this Figure we can clearly see that the minima on the curves corresponding to $^2B_2$ and $^2A_1$ symmetries are very close to each other in terms of energy (on the order of 200 cm^{-1}). Hence it is might not be immediately clear to which state corresponds the global minimum of the system. With *ab initio* calculations we found that the systems Li_2Cs, Na_2Li, Na_2K, Na_2Rb, Na_2Cs, K_2Li, Rb_2Li, Rb_2K i Rb_2Cs have the equilibrium geometry C_{2v} corresponding to the state $^2B_2$. In other cases: Cs_2Li, Li_2Na, K_2Na, Rb_2Na,Cs_2Na, Cs_2K, Cs_2Rb, Li_2K, Li_2Rb, K_2Rb, K_2Cs, Rb_2Na there is further distortion to the C_s state, in which the trimers states exhibit similar character to the $^2A_1$ state.

Rysunek 2: Potential energy curves of $^2B_2$ i $^2A_1$ states of ARb_2 systems, corresponding to the minimum energy for fixed angle.



The *ab initio* calculations of potential energy surfaces in AB_2 systems demonstrated, that in all investigated systems the energy needed for trimer formation is much higher than the dissociation of two AB molecules, hence the chemical reaction of trimer formation is energetically forbidden. We can also conclude that in case of A+AB collisions, the potential is very deep, and there is no barrier between initial channel A+AB and the colliding complex. In such case the AB_2 system supports a lot of bound states and the collisions are strongly dominated by (Feshbach) resonances, similarly as the system Rb+ND_3 (cf. Section 4.4).

For the long separation between two subsystems AB+AB or A+AB the potential can be represented by the expansion $V(R) \approx C_6 R^{-6} + \ldots$. The C_6 coefficients are referred to as the van der Waals coefficients. At present rigorous quantum scattering calculations for such systems are impossibly difficult, however, approximate models for such scattering were developed recently, for example quantum defect theory of Idziaszek and Julienne [22]. The crucial parameter in all simplified theories, which governs the attraction of colliders is always the C_6 coefficient. It also determines the density of states near the dissociation limit, density of scattering resonances, height of the centrifugal barriers etc.

The publication **[H2]** completes the study presented above: it includes the study of C_6 coefficients for the interaction of A+AB and AB+AB systems when molecules are in their rovibrational ground state. The C_6 coefficients in these systems consist of two contributions, dispersion and induction. The first contribution can be calculated from the dynamic polarizabilities of atoms and molecules, integrated over the imaginary frequencies, according to the equation [23]:

$$C_6^{\mathrm{disp}} = \frac{3}{\pi} \int_0^\infty \bar{\alpha}_X(iu)\bar{\alpha}_Y(iu)du \qquad (1)$$

where $\bar{\alpha}_{\rm mol}$ is the isotropic polarizability od molecule X (or atom X). Second, induction, contribution is the product of the dipole moment and molecular (or atomic) isotropic polarizability in static limit:

$$C_6^{\rm ind} = \mu_X^2 \bar{\alpha}_Y(0) + \mu_Y^2 \bar{\alpha}_X(0). \quad (2)$$

In addition to that, in molecular system AB+AB with small rotational constant one can show, that there exists second-order [24] contribution to the C_6 coefficient given by $\mu^4/6B$ (μ - dipole moment of AB, B - rotational constant).

To determine the C_6 coefficients we evaluated the dynamic polarizabilities of appropriate molecules using the time-independent coupled cluster polarization propagator [23, 25]. For atoms we used recently published polarizabilities by groups of Derevianko and Babb [26]. The dipole moments were calculated using the finite field method.

The systems A+AB have a very diverse values of van der Waals coefficients: for the systems Li+LiX they are between 2223-4192 a.u. (for X=Na-Cs), which is about 5 time less than for Cs+CsX systems (9455-1882 a.u.). The contribution of induction to the C_6 is large only for the systems with molecules with large atomic size difference: LiCs, LiRb, LiK, NaCs - in those cases it can be on the order of 20%. Using the C_6 coefficients we have evaluated the barrier heights for the p and d partial waves, which determine the limit for single partial wave dominated s-wave regime (assuming AB molecules are bosons). It turns out that in A+AB systems the temperature dominated only by a single partial wave for A=Li corresponds to 1.3-2 mK, for A=Na,K in the range 100-600 μK. For the heavy systems containing two Rb or Cs atoms it is on the order of tens of microkelvins.

4.3 Magnetoasociation of alkali-metal atoms and closed-shell atoms

Association of atoms with time-varying magnetic field is possible if one employs the Feshbach resonances. To this end the magnetic field is being swept across the resonance, so that the system switches from the scattering state to the bound state. The resonance in given scattering state is produced by tuning the Zeeman shift of atom energy levels with energy levels of bound states of diatom. In such way it is possible to tune the scattering length of the system, as well as associate the atoms to the molecules. For the first time the applications of Feshbach resonances were suggested by Tiesinga and coworkers [27] in 1993. In 1998 the group of Ketterle observed the Feshbach resonance in ultracold Na_2 ultracold gas [28]. Since then the Feshbach resonances are one of the most important tools used to control the interactions in the ultracold gases.

In case of alkali-metal atoms there are two mechanisms which can drive the Feshbach resonances: the first is related to the difference between the triplet and singlet interaction

potentials - such mechanism yields strong resonances, the second is simply electronic spin-spin dipolar interaction - such effect gives much weaker resonances. *None* of these effects is present in case of interaction of alkali-metal atoms with close-shell atoms and one has to reinvestigate the system to identify possible coupling mechanisms. The paper **[H2]** focuses on search for new mechanisms of Feshbach resonances for prototype Rb+Sr system.

Using quantum chemistry methods we analysed the possible effects in RbSr molecule that might drive the Feshbach resonances: the coupling of electronic spin (s_{Rb}) with nuclear spin (i_{Rb}), electronic spin with rotations, nuclear spin with rotations, nuclear spin with electric field gradient of molecule, etc. Among all these effect the modification of hyperfine coupling induced by the interaction is by far the strongest effect. The interaction distorts electronic cloud on Rb and the spin density on nuclei, so the hyperfine coupling between i_{Rb} and s_{Rb} is reduced by about 20% from its asymptotic value (hundreds of MHz for Rb). As a result, the scattering (atomic) states experience different mixing of spin i_{Rb} and s_{Rb} than molecular (bound) states of RbSr. Such effect causes the Feshbach resonances. Other effects are on the order of 20 MHz (eg. electron spin-rotation) or less (nuclear spin-rotation, anisotropic hyperfine interaction). We have also calculated the interaction potential for RbSr using open-shell version of coupled clusters method with singly-, doubly- and triply excited amplitudes [RCCSD(T)] [29].

To study the scattering in RbSr system we used close-coupling equations and the basis set in which the quantum numbers are m_s and m_i – the projection of electronic and nuclear spin onto the lab-frame axis (defined by B-field direction). Since the total spin $m_f = m_s + m_i$ is conserved, the basis set is restricted to two scattering channels $m_f \pm \frac{1}{2}$. The propagation of close-coupling equation (for the collision energy of 1 nK) allows to calculate the scattering matrix and the scattering length. We determine the crucial parameters of resonances – the width Δ_{r} and position B_{r} by fitting to the analytical form $a(B) = a_{\mathrm{bg}}(1 + \Delta_{\mathrm{r}}/(B - B_{\mathrm{r}}))$. Far from the resonance we determine the background scattering length a_bg.

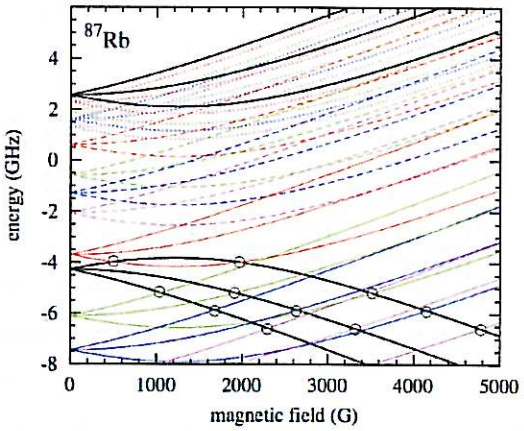
The Hamiltonian of the system RbSr can be written as

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \zeta \mathbf{I}\cdot\mathbf{S} + \mu_B g_e \mathbf{B}\cdot\mathbf{S} + \mu_B g_n \mathbf{B}\cdot\mathbf{I} + V(R) + \Delta\zeta(R)\mathbf{I}\cdot\mathbf{S} \tag{3}$$

where the first term is the kinetic energy of the system ($\hat{p}$ is the relative momentum of the system, μ is the reduced mass), the second term describes the atomic coupling of nuclear spin of Rb and electronic spin (ζ = 1.013 GHz for ^{85}Rb and 3.4 GHz for ^{87}Rb). The third term denotes the Zeeman interaction of spins with the magnetic field (μ_B is Bohr magneton, g_e i g_n, gyromagnetic factors), while two last terms represent the distant-dependent interaction terms: Born-Oppenheimer potential and modification of hyperfine coupling at short range.

Feshbach resonances are produced for the fields where the open channel energy (lower m_f state) is identical to the bound state energy of open-chennel (upper m_f state). Thus, the

Rysunek 3: Energy levels of the rubidium-87 atoms in magnetic field (black lines) with colour-coded molecular states supported by the closed-channel (correlating with $f = 2$ in zero-field). Molecular states correspond to all isotopes of the Sr atom. With circles we mark the positions of resonances, which are located where the lines of the same m_f intersect.



resonances are driven by the vibrational states with binding energy comparable to the hyperfine splitting. The calculations have been performed for all possible isotopic combinations of Rb and Sr atoms in the system, so in a way, we explore the behaviour of resonances for different background scattering lengths. The Figure (4.3) shows the positions of resonances for all isotopic combinations of ^{87}RbSr.

To evaluate the exact form of the coupling one needs to transform the matrix elements of the $\Delta\zeta(R)\mathbf{I}\cdot\mathbf{S}$ operator to the basis of eigenstates of asymptotic Hamiltonian. After some algebra one can show that the coupling between channels takes the following form :

$$\tilde{V}(R) = \frac{\Delta\zeta(R)\mu_B g_e B}{4}\sqrt{\frac{(1+2i)^2 - 4m_f^2}{\zeta^2(1+2i)^2 + 16\zeta m_f \mu_B g_e B + 16\mu_B^2 g_e^2 B^2}} \tag{4}$$

The coupling is linear in B-field and saturates for very large field, on the order of ζ/μ_B. The width of resonances at low field must be low, since it depends quadratically on $\tilde{V}(R)$.

The Table (1) contains selected resonances for various mixtures of RbSr systems. These systems have a different background scattering lengths. According to our expectations, for very small fields the resonances are very narrow and unlikely to be practically used in magnetoassociation (for example ^{85}Rb^{88}Sr at B=37 G). Resonances are broader for negative m_f because of stronger i_{Rb} and s_{Rb} mixing. If the background scattering length is large (ca. 1000 Å) or small (ca 1 Å) the resonances can be as large as 0.01-0.1 G. This is enough for their

Tablica 1: Example parameters of Feshbach resonances in Rb+Sr system for various isotopic mixtures.

uklad	B_r (G)	a_{bg} (Å)	Δ_r (mG)	m_f
^{85}Rb^{84}Sr	1797	95	-0.16	+2
	1108	95	-0.59	-2
	336	95	0.055	-2
^{85}Rb^{88}Sr	37	56	0.00003	+2
	792	56	-0.27	-1
^{87}Rb^{84}Sr	477	1715	7.4	-1
^{87}Rb^{86}Sr	1896	55	-1.1	0
^{87}Rb^{88}Sr	2281	1.6	-34	+1

applications in control of quantum gases or magnetoassociation.

4.4 Cold collisions of atoms and molecules: interaction potentials, resonances and sympathetic cooling

In this Section we present the detailed discussion of problems related to atom+molecule scattering in low-energy limit presented in publications **[H4–H8]**. The common idea of these works is modelling of the atom+molecule collisions from first principles. That relies on calculations of interaction potentials followed by quantum scattering calculations. Here, we present the publications devoted to the interactions of I and II group atoms with ammonia and NH, modelling of the low-energy collisions of ammonia+Rb, study of interactions and collisions in N+NH system and metastable helium with H_2 and Ar.

4.4.1 Interactions of group I and II atoms with ammonia and NH molecules

The papers presented in this part contain the *ab initio* studies of the interaction surfaces of alkali-metal atoms and alkaline-earth atoms with ammonia and NH molecules. The molecules of our interest are one of the most important in the field: both have been decelerated with dynamic electric field [30, 31], while cold NH (0.1-1 K) molecules were studied in buffer-gas cooling experiment [32].

Modelling of the low-energy collisions requires the knowledge of the interaction potential. In cold matter physics the relevant systems almost always contain open-shell systems. *Ab initio*

calculations for these systems are always a challenging task. In particular, in such systems, a strong coupling between ground- and excited states can occur, for some geometries the states might exhibit conical intersection or avoided crossings – if they belong to the same symmetry. Still, very little is known about these systems: the full potential energy surface for group I and II atoms with ammonia molecule has been obtained for the first time in one of papers included here [**H3**]. Among atom+NH systems, very preliminary, qualitative studies of Rb+NH have been performed by Soldan and Hutson [33].

Pre-cooled molecules can be trapped in electric or magnetic in the so-called low-field-seeking state, which is not a ground state. In the inelastic collisions, the kinetic energy is released and usually the amount of such energy is able to remove the molecule from trap, which is usually very shallow. The main coupling term that couples the energy levels of molecule (rotational, Zeeman or Stark levels) in collision process is the anisotropy of the interaction potential. If the anisotropy of the potential is larger than the rotational constant of a molecule the coupling is very strong and the collisions have strongly inelastic character. Hence, the main feature of the potential energy surface in atom+molecule system we pay attention on in papers [**H4**, **H5**] is its anisotropy.

To study the potential energy surface of atom+ammonia systems we employed the RCCSD(T) method. For Li, Na, Be and Mg atoms we included all electrons in the calculations, while in the remaining cases we have used the effective core potentials to describe inner shells of atom [34]. We have also studied the interaction of Xe atom with ammonia, a very hot topic system in benchmarking the velocity-selected and cold collisions (through the Stark deceleration). In the paper [**H4**] we have calculated the full potential for Rb+ammonia and Xe+ammonia systems, while for other systems we characterised the minima in the systems, which is enough to figure out the information about anisotropy. We have also found the Van der Waals coefficients in studied systems.

In all systems containing metals interacting with NH_3 the interaction potentials exhibit very strong attraction from the side of lone pair of molecule: from 884 cm^{-1} for Mg atom to 5104 cm^{-1} for Li atom. Interaction of group II atoms other than Mg with ammonia resembles more alkali-metal atoms: the depth of minima near the nitrogen atom are on the order of 2000-3000 cm^{-1}. For the alkali-metal atoms the depth systematically decreases from Li to Rb atoms. A secondary minima in all these systems are placed on C_{3v} axis of a molecule, from the side of hydrogen atoms. These minima are very shallow in each case - on the order of 100-120 cm^{-1} - and they originate from Van der Waals forces, a balance between exchange and dispersion energy. Hence, the interaction potentials in case of group I and II atom+molecule systems are very strongly anisotropic. Even without doing any scattering calculations we can guess, that rotationally excited molecules should be collisionally unstable in the electrostatic traps. The

role of anisotropy of potential on the collisional stability of $j = 1$ state of para-ammonia is, however, less clear.

The interaction potential of Xe+ammonia system has completely different character: it is a typical example of Van der Waals system dominated by dispersion forces. The anisotropy in this system is small, just few times larger than rotational constant of ammonia, while the global minimum in this system is 173.5 cm^{-1}. The equilibrium geometry of this system is T-shape.

The studies of potential energy of atom+NH systems are particularly difficult, because of previously mentioned intersections of excited state with the ground state. As a matter of fact, the neutral state in the linear geometry, atom+NH, intersects with ion-pair state $atom^+NH^-$, and the crossing occurs at about 3-4 Å. The ion-pair state at long range is an excited state, while at short-range its depth is on the order of 10000-20000 cm^{-1} (1-2 orders of magnitude more than the depth of neutral state). Initially we have examined the systems only for the linear geometries, for which it is much easier to calculate the interaction energies with state-of-the-art *ab initio* methods, as the symmetries of atom+NH and $atom^+NH^-$ states are different. For these geometries we have determined accurately the positions of crossings of these states with the coupled cluster method. Except Mg+NH and Be+NH systems these crossing occur for the negative energies with respect to the Be+NH and Mg+NH thresholds. Hence, the ionic state surface is energetically accessible for the collisions. The anisotropy in such case will be extremely large, on the order of 10^4 cm^{-1}. That is very likely to increase the inelastic cross-sections in these systems.

The intersection of ionic and neutral states for Be+NH and Mg+NH systems occurs at the energies which are +1500 cm^{-1} above the entrance channel atom+NH, hence, the ionic state is separated from the neutral state with a barrier, non-penetrable for low-energy collisions. In these systems the anisotropy of neutral state is very small, on the order of 10 cm^{-1}. Since the CCSD(T) calculations for the full potential energy surface are not possible because of close vicinity of excited states in C_s geometry, we have employed the symmetry-adapted perturbation theory (SAPT) to calculate the global potential energy surface of Mg+NH system. Since the beryllium atom is not a subject of present experimental efforts, we have restricted ourselves only to Mg+NH system.

The perturbation theory allowed us to calculate the full-dimensional interaction potential. For linear geometries we could compare the SAPT and CCSD(T) performance to cross-test these results. The agreement between these methods is good for linear geometry: the well depths difference is on the order of 9%. The SAPT potential energy surface has two minima: 92 cm^{-1} and 113 cm^{-1} separated with a barrier of about 24 cm^{-1}. The anisotropy of the potential in this case is on the order of rotational constant of NH (16 cm^{-1}), which means

that the coupling in the scattering Hamiltonian is weak and the collisons in this system should favour elastic collisions.

4.4.2 Cold collisions of Rb with the ammonia molecule

In the paper **[H6]** we continued research started in Ref. **[H4]**. Using the potential energy surface for Rb+NH_3/ND_3 we were examining the cross section for the collisions in these systems. We assumed that NH_3 and ND_3 molecules are in their $j = 1$, $k = 1$ state, where j is the total angular momentum of ammonia, and k is its projection on symmetry axis of the molecule. Since the potential energy of isolated molecule exhibit double minimum as the hydrogen atoms are moved along the C_{3v} axis, the rotational levels of ammonia are split into the so-called inversion doublet (or tunnelling doublet): for the NH_3 molecule the inversion splitting is 0.8 cm $^{-1}$, while for ND_3 0.05 cm^{-1}. These states are labelled with three quantum numbers: $|j, k, u/l >$ where the u/l denote appropriate component of tunnelling splitting (upper and lower). The state $|1, 1, u >$ in electric field splits further into one state which is low-field-seeking trappable state. Thus, the state $|1, 1, u >$ is essential for studies of cold collisions of ammonia.

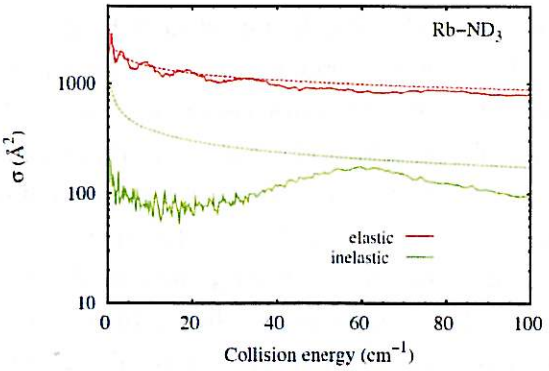
We have studied the broad range of collision energies: from ultracold (10^{-7}K – 1K) to cold regime (do 140 K=100 cm^{-1}) using the close coupling method. In higher temperatures the number of partial waves needed, increases the complexity of problem, thus in these temperatures we have employed the coupled states method of Green [35].

The system Rb+ammonia exhibit a very large anisotropy of the potential, and a lot of rotational states of ammonia $|j, k, u/l\rangle$ had to be included into the close coupling basis set to achieve the convergence.For the ND_3 molecule the basis included the states up to $j = 21$ while for NH_3 up to $j = 14$.

Despite the large anisotropy of the potentials, both Rb+ammonia systems turned out to be not so strongly affected by inelastic collisions. In the Figure (4.4.2) we have shown the elastic (red line) and the total inelastic cross section for the initial state $|1, 1, u\rangle$. The dashed green line denotes the Langevin limit for the inelastic collisions, which is one order of magnitude larger than the one which results from rigorous quantum scattering calculations. For the collision energies on the order of 50 cm^{-1} the contribution to the inelastic collisions originates not only from the relaxation to $|1, 1, l\rangle$ state but also from the collisionally induced rotational excitations of ammonia molecule: $|1, 1, u\rangle \rightarrow |2, 1, u/g\rangle$ and $|1, 1, u\rangle \rightarrow |2, 2, u/g\rangle$.

In ultracold and cold collisions it is particularly important to understand the resonances in the scattering, and the Rb+ND_3 system is a good prototype for such study. In the paper **[H6]** we have carefully analysed their origin and behaviour in the lowest partial waves. Both, elastic and inelastic cross-sections have a very dense resonant structure. Resonances in the elastic scattering are small compared to the nonresonant background and strongly diffused,

Rysunek 4: Elastic (red line) and inelastic (green line) cross-sections from the $|1,1,u\rangle$ for the range of energies 0-100 cm^{-1}. The dashes red line denotes the semiclassical background scattering model, the dashed green line - the Langevin limit for the inelastic collisions.



which contrasts with resonances in the inelastic scattering. For low collision energies (up to 20 cm^{-1}) the resonances in the inelastic cross section are very sharp and much stronger than the background. In fact the inelastic scattering is dominated by resonances. The rubidium atom and ammonia molecules attract each other very strongly (C_6 coefficient is very large) and the centrifugal barriers are very low. The resonances are dominated by Feshbach resonances which originate from rotationally excited ammonia molecules (with $j > 1$) bound with Rb atom.

For the Rb+ND_3 we have studied also the cross-sections for the $|1,1,u> \rightarrow |1,1,l>$ relaxation in the ultracold limit (down to 0.1 μK). Below the collision energies of about 100 μK the cross-sections are already in the Wigner regime: the elastic cross section tends to the constant value, while the inelastic cross section tends to infinity as $E_{\mathrm{coll}}^{-\frac{1}{2}}$ (E_{coll} is the collision energy). The crucial in the sympathetic cooling is the ratio of elastic to inelastic cross-sections. For the potential considered here this is on the order of 10, which possibly is not enough for efficient sympathetic cooling of ammonia.

The best *ab initio* methods, such as CCSD(T), used nowadays in studies of molecular interactions are limited in their accuracy. For simple, few-electron system they can achieve 1-2% accuracy. In the present study, in which the rubidium is described with the effective core potential, the accuracy is probably much smaller. Thus, we have investigated the elastic and inelastic cross-sections of Rb+ND_3 system for the collision energies 10 μK, for the family of potentials obtained from the original one by scaling it $V(R) \rightarrow \lambda V(R)$ with the λ parameter between 0.99 and 1.01. The effect of potential scaling on the cross-sections is shown in the

Rysunek 5: The cross section for Rb+ND_3 collisions, elastic (red line) and inelastic (green line) for the collision energy 10 μK as a function of scaling parameter λ for interaction potential.

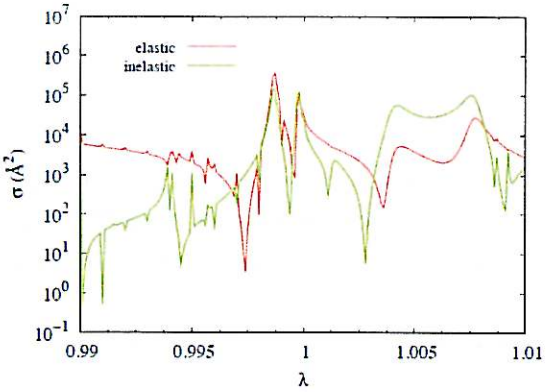


Figure (4.4.2). Within studied range of λ the cross-sections change drastically by many orders of magnitude. The main reason for such behaviour is the position of the top bound state of Rb+ND_3 ($j = 1$) system: if the bound state is right at the threshold, we observe huge increase of both cross-sections - note the clear feature near $\lambda = 0.999$ in the Figure (4.4.2). Superimposed on that are additional, numerous, sharp Feshbach resonances which originate from quasibound states of Rb atom with the excited ammonia in rotational states $j > 1$. Albeit the cross-sections depend dramatically on the potential, the ratio of elastic to inelastic cross-sections is fairly independent on it, typically below 100 (which is unfavourable for sympathetic cooling). The sensitivity of the cross-sections for the potential energy surface decreases for higher energies and partial waves. Accurate, quantitative predictions of the cross-sections, especially near the resonances, are thus, very challenging.

4.4.3 The N+NH system: the interactions and cold collisions in the magnetic field.

Since the nature of N+NH interaction is completely different compared to metal+NH, I have decided to devote a separate section to this problem. Co-trapping and mutual cooling of NH with N has been investigated by Doyle's group (Harvard) in 2009. The nitrogen molecules are light, have small polarizability and interact with molecules rather weakly at long range (due to a small C_6). Hence, the centrifugal barriers in this system are high compared to the systems like Li/Cs+NH or Mg/Sr+NH. Inelastic collision cross section is proportional to the integral $\int dr \psi_{\mathrm{i}}^{E}(r) V_{\mathrm{cpl}}(r) \psi_{\mathrm{f}}^{E'}(r)$, where $V_{\mathrm{cpl}}(r)$ is the coupling between the channels,

$\psi_{\mathrm{i}}^{E}/\psi_{\mathrm{f}}^{E'}$ is the radial wavefunction for the initial/final scattering state with incident energy E and kinetic energy release E'. If the final state corresponds to the partial wave L and released kinetic energy is smaller than the centrifugal barrier this integral is small, since the short-range amplitude of $\psi_{\mathrm{f}}^{E'}(r)$ is small.

In the paper **[H7]** we described the new potential energy surface for the high-spin N+NH system with estimated accuracy of about 2%, obtained with CCSD(T) method. For the light atoms the gaussian basis sets are well optimized: this allowed us to nearly eliminate the inaccuracy attributed to basis set incompleteness. The potential energy surface of N+NH system supports 5 bound states, its depth is about 90 cm^{-1} with global minimum in linear N–N–H configuration. Because of that, the cross-sections are much less sensitive to the potential energy surface modifications.

In scattering calculations we have used the following Hamiltonian for the nuclei dynamics:

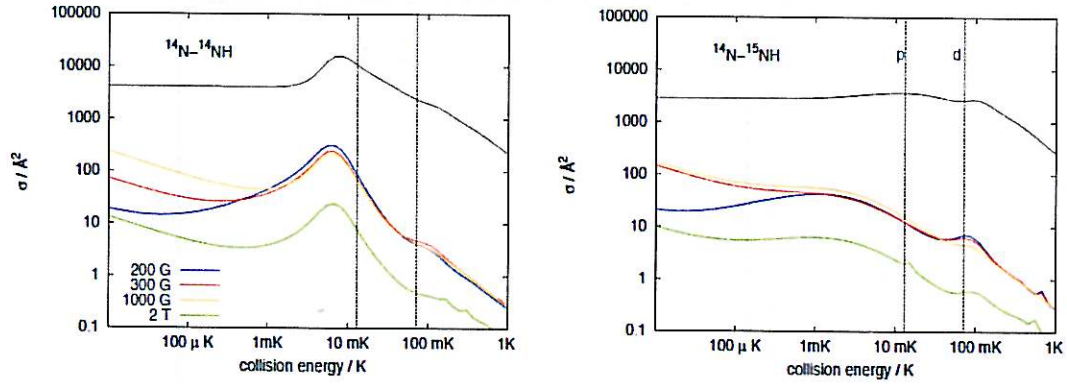
$$\widehat{H} = -\frac{\hbar^2}{2\mu R^2}\frac{d^2}{dR^2}R + \frac{\hat{L}^2}{2\mu R^2} + H_{\mathrm{NH}} + H_{\mathrm{Z}} + V_{\mathrm{SS}} + V_{\mathrm{int}}(R,\theta) \tag{5}$$

where $\hat{L}$ is the end-over-end angular momentum operator, H_{Z} is the Zeeman Hamiltonian, V_{SS} is the spin dipole interaction between NH and N, while V_{int} is the electronic Born-Oppenheimer interaction of N i NH. The operator H_{NH} is the internal Hamiltonian of NH molecule containing the rotational term and intramolecular spin-spin interaction. In the magnetic field, the projection of total angular momentum of a system onto the axis of the field B is conserved, in other words $M = m_s(\mathrm{N}) + m_s(\mathrm{NH}) + m_L + m_n(\mathrm{NH})$, where $m_s(\mathrm{N})$ and $m_s(\mathrm{NH})$, m_L, $m_n(\mathrm{NH})$ are the projections of pertinent angular momenta - spin s, of N and NH, end-over-end angular momentum L, rotational quantum number n of NH – onto the B field axis.

The initial energy level considered here was the ground rotational state of NH $n = 0$, $m_n = 0$, with highest possible electronic spin projection of the system N+NH: $m_s(\mathrm{N}) = \frac{3}{2}$ and $m_s(\mathrm{NH}) = 1$. Such state is magnetically trappable. Rate of inelastic collision to lower Zeeman states (so-called Zeeman- or spin relaxation) determines the stability of a mixture in the magnetic trap. We investigated the collision energies from 10 μK do 1K, for which it was needed to include the partial waves up to $L = 5$. All isotopes of nitrogen in N+NH systems were considered. We also studied the magnetic fields of experimental interest: below 300 G, but also as large as 0.1 and 2 T.

The main result of this paper is the energy dependance of the cross-sections for all isotopic combinations of N+NH system in the system, shown in the Figure (6) for two example isotopes of N. Regardless the magnetic field, the key role in spin relaxation is due to spin-dipole interaction, rather than rotational coupling. For each isotopic mixture we have obtained large ratio of elastic to inelastic cross-sections for all investigated collision energies. For the small fields, this is caused by centrifugal suppression, which is depicted in the Figure (7). There are

Rysunek 6: Elastic (black line) and inelastic (color-coded lines for various magnetic fields) as a function of collision energy for two example isotopic mixtures of N+NH system. Vertical lines denote positions of centrifugal barriers p and d. Note the strong p-wave shape resonance for ^{14}N-^{14}NH.



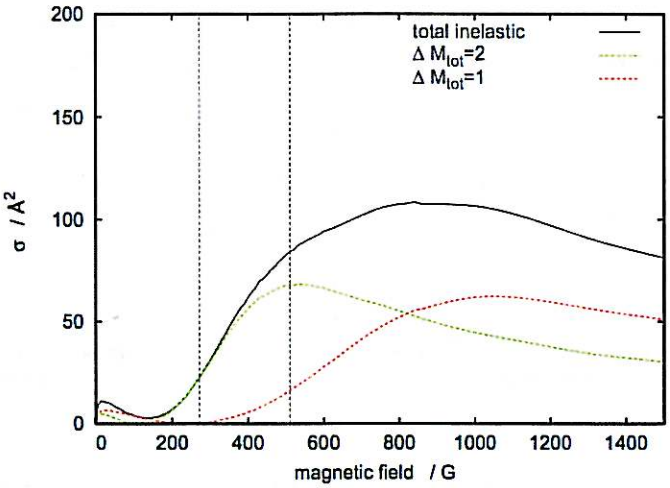
two outgoing channels for the initial channel with maximum spin and $L = 0$ corresponding to two different Zeeman levels. If the Zeeman splitting between initial and final state is larger than the corresponding $L = 2$ centrifugal barrier the inelastic cross section increases. Very high magnetic field (on the order of 1 T) one can also suppress the inelastic cross section, because of a large energy gap between initial and final state.

In ^{14}N+^{14}NH we observed a very strong p-wave shape resonance in elastic and inelastic cross-sections. We found, that it is because of a shape resonance which can be easily found in isotropic part of the potential. We explored the inaccuracy of our CCSD(T) potential and studied the cross-sections by scaling it within expected uncertainty. It turns out that such sensitivity is rather small and we always predict the strong p-wave Feshbach resonance near 10 mK.

4.4.4 Cold collisions of the metastable helium with H_2 and Ar

Theoretical studies of the collisions in the N+NH system shown that for the light systems (with small reduced mass μ), with shallow interaction potentials and few bound states, theory can quantitatively predict the low-energy cross-sections, as they are much less sensitive for details of the interaction potentials. One of the most interesting systems, which is recently studied experimentally, is metastable helium colliding with various closed-shell species, in particular the argon atoms and the hydrogen molecule. In 2012 Narevicius and coworkers [17] for the first time studied the collisions with the ultralow collision energy (10 mK–few K: from

Rysunek 7: Total inelastic (black line) cross-sections and its state-to-state components (color coded) as a function of magnetic field for the collision energy of 100 μK, for the $^{14}N+^{14}NH$ system. Vertical lines correspond to the fields for which the Zeeman shifts of final states are equal to the centrifugal barrier heights in p and d waves.



pure s-wave regime up to a few partial waves) in unprecedented details. These collisions are reactive: because of the large internal energy of He* atom (20 eV) the collisions cause the autoionization of the whole system - this process is referred to as the so-called Penning ionization. The full description of the Penning ionization is extremely challenging, however to characterise the resonances in these collisions we only need to know precisely the potential of the entrance channel. The studies of entrance-channel potential is given in the paper [**H8**] from the presented collection of publications.

The calculations of the potential energy surfaces for the systems containing He* are very challenging. The quantum chemistry methods work very well for the systems in their ground states for given spin/symmetry combination. This is not the case for Penning-ionizing systems – the system A*+B is submerged in the continuum of ionized states AB^++electron, which can have severe effect on convergence of the self-consistent field equations, which essential step before much more accurate study with coupled-cluster method.

In the paper [**H8**] our attention was focused on the systems He*+H_2 and He*+Ar. We have also studied the systems with metastable neon, which is also interesting for future experiments in the field, however, no scattering calculations for these systems have been performed.

We employed two independent methods to study the interaction potentials. First, the

CCSD(T) calculations for He^*+H_2 and He^*+Ar were performed with carefully prepared starting orbitals. The Hartree-Fock orbitals in the first step were obtained for the isolated monomers and merged, afterwards. We also carried out the symmetry-adapted perturbation theory calculations (SAPT) according to the methodology presented in the Ref. ([36]). The use of the SAPT method serves mainly as a test of CCSD(T): the SAPT itself is the perturbation series with neglected third- and higher terms in the interaction potential, hence it is expected to be less accurate. Nevertheless, the methods agree to within 15%. The depths of the potentials calculated with CCSD(T) method are 12.9 cm^{-1} and 27.3 cm^{-1} for He^*+H_2, and He^*+Ar respectively.

The most important test of both methods is the comparison of experimental and computed positions of shape resonances in cross-sections for the Penning ionization. Since the resonances depend only on the entrance channel it was possible to check their positions only in the elastic cross-sections. To this end we explored the collision energies in the range of 10^{-3} meV – 1 meV (0.01–10 K). Both, CCSD(T) as well as SAPT potentials, predicted similar cross-sections within this range. In Narevicius' experiment the resonances in Penning ionization in the He^*+H_2 system, were found at the collision energies 0.02 i 0.2 meV. For the CCSD(T) potential these positions are at the energies of 0.08 and 0.3 eV, while the SAPT potential yields 0.1 and 0.3 meV, respectively. For the He^*+Ar system the experimentally found resonances were located at 0.1 and 0.3 meV, whereas both, the SAPT, and the CCSD(T) potentials predicted their positions at 0.2 and 0.4 meV. Given the great sensitivity of the positions of the resonances in the cross section on details of the potential energy curve, the agreement of this pioneering calculations with experiment is very satisfactory.

4.5 Summary and impact of the publications

Theoretical studies of the interactions and collisions in ultracold gases are essential to point out further courses of experimental research and to help understand them. The results gathered in the publications presented here answered several most urgent questions posed by leading experimental groups in the field, regarding the formation of new sorts of molecules, their stability and nature of their collisions. The papers discussed here combine pioneering, multidisciplinary study on the frontier between chemistry and physics.

In summary, once more I would like to point out the most important conclusions following from the research presented in the collection of publications presented here.

- The *ab initio* calculations employing quantum chemistry methods demonstrated, that the quantum gases of alkali-metal dimers are collisionally stable with respect to trimer formation, while all the molecules containing Li atoms and the KRb molecules undergo the atom exchange reaction and are collisionally unstable. These conclusions should guide

the experiment to choose appropriate atoms so that the production of molecular Bose-Einstein condensate, as a long-standing goal, is possible. The calculations we performed have explained the structure of AB_2 systems (with A and B being alkali-metal atoms) and shown, that there exists intersection between the ground and excited states of the system very close to its energy minimum. The calculations of the Van der Waals coefficients in the A+AB and AB+AB systems have shown that they are very large in magnitude. This results in large attraction of these molecules, large density of vibrational states near the threshold and large density of the Feshbach resonances in the scattering, originating from the excited states of molecule.

- We explored the Rb+Sr system, for which a very careful *ab initio* analysis of hyperfine and fine effects in the interactions of Rb and Sr atoms were performed. The quantum scattering calculations, shown that for certain magnetic fields it is possible to observe a Feshbach resonances in this system. Hence, the magnetoassociation and magnetic-field control of interactions in these atoms is possible. This opens up entirely new opportunities of studies in the field and should encourage the experimentalists to study mixtures of atoms with different spin quantum number.

- *Ab initio* calculations of the potential energy surfaces of the I and II group atoms with ammonia shown, that in these systems the anisotropy of the interaction is very large compared to the rotational constant of ammonia. A very strong anisotropies are also present in the systems Li/Cs+NH, Sr+NH and Ca+NH, mostly due to a very strong ion-pair character of the interaction. On the other hand, the interaction of Be and Mg atoms with NH is very weakly anisotropic and of the non-covalent (Van der Waals) nature.

  Thus, Mg+NH is might be a good candidate for sympathetic cooling of NH molecule.

- Using the potential energy surface of the Rb+ammonia system, we performed the quantum scattering calculations of cross-sections for the initial state $|1,1,u>$ of ammonia, which is trappable. For the collision energies near 1 K and above the inelastic collisions are smaller than expected - they are small compared to the Langevin limit by 1-2 orders of magnitude, dominated by a dense Feshbach resonances. In the ultracold limit the inelastic cross section for $|1,1,u> \rightarrow |1,1,l>$ process are very large compared to the elastic ones. It is quite unlikely that ultracold Rb atoms can sympathetically cool the ammonia atoms by collisions.

- It turns out that the nitrogen atoms can efficiently cool the NH radicals. In the presented quantum scattering calculations employing newly obtained *ab initio* potential energy

surface of high-spin N+NH we have demonstrated that the collisionally induced Zeeman relaxation is quite unlikely. For the low magnetic B fields the outgoing channel wavefunction is suppressed by a centrifugal barrier, while for a very fields (on the order of 1 T) the energy gap between initial and outgoing channels decreases the inelastic collision rate.

- The collision properties of the He^*+molecule system can be reliably predicted from the *first principles*. In particular we can predict the positions of shape resonances which are responsible for increase of the Penning ionization rate in a few lowest partial waves.

The crucial step in the above papers was to obtain the potential energy surfaces in appropriate atom+molecule or atom+atom systems, employing the quantum chemistry methods. We have explored the sensitivity of the collision properties on the shape of the potential surface. Interestingly enough we have found, that the systems with large reduced mass, deep potential, hence, with a large number of supported bound states, the sensitivity of cross-sections to the modification of the potential is very large. On the contrary, for the systems with small reduced mass, shallow potential and small number of supported bound states the sensitivity is much smaller and the *ab initio* methods of quantum chemistry are able to predict the scattering length and cross-sections. For the systems with large number of bound states such study can only be qualitative and the discussion of the results should always be assisted by exploring the potential dependance.

The publications presented here had a very strong impact on the field and direction of research on cold molecules. The paper **[H1]** has stated what molecules should be subject of study to achieve the molecular quantum degenerate gas: at present there exist ongoing research on formation of several alkali-metal dimers, such as RbCs, KCs and KNa. This paper has been cited more than 60 times in recent four years. The publication **[H3]** has also significantly changed the course of research on ultracold matter. Since 2010 several experiments has been launched in which it is planned to produce the paramagnetic and polar molecules, in particular YbCs (Durham University), YbLi (Seattle, Kyoto), RbSr (Innsbruck/Amsterdam), He^*Rb (Amsterdam), HgRb (Torun). Since the publication year the work has been cited over 30 times. The papers **[H4]** and **[H6]** (each of them has been cited about 30 times) are so far the only study of quantum scattering for such strongly anisotropic, heavy and strongly attractive system. In the publication **[H6]** it was for the first time shown, that low-energy collisons of heavy, strongly attracting systems are strongly affected by Feshbach resonances. One of the most important outcomes of these works was the common paper with the experimental group of Heather Lewandowski (from JILA laboratory) devoted to the effect of electric field on the Rb+ND_3 cross-sections, in temperatures on the order of 0.1 K [11]. This publication has confirmed strongly inelastic character of the collisions in cold regime. Also, the papers devoted

to the collisions of NH molecule have gained a lot of attention in the field. For the Mg+NH system the spin relaxation in the magnetic field has been theoretically explored and it was found, that such system is suitable for sympathetic cooling [37]. The publication **[H7]** inspired further research on collisions of molecules with very light atoms (like Li or H) [38, 39]. Soon after publishing **[H7]**, Doyle and his group have confirmed our findings for the temperatures above 100 mK [40]. Finally, I have established collaboration with prof. Narevicius group soon after publishing the paper **[H8]**. Using the potential published in **[H8]** we have predicted accurately the shape resonances in the analog systems to $He^* + H_2$: $He^* + D_2$ and $He^* + HD$. The paper was first demonstration of the impact of isotope effect on chemical reaction and appeared in Nature Chemistry in the beginning of 2014 [41].

5 Discussion of other scientific achievements.

Apart from the publications presented in the previous section, my scientific activity since 2007 (year of awarding my PhD degree) was focused on two areas: first, I was involved in further research on cold matter physics and cold molecules. Secondly, I focused on applications and development of new *ab initio* methods for studying the intermolecular forces. In this section I will briefly describe my most important achievements in these areas.

5.1 Ultracold physics and chemistry

The main research in this field was focused on the following topics:

- **Theoretical and experimental studies of the collisions Rb+ND_3 in the electric field.**
  Sympathetic cooling of the ammonia molecules by collision with ultracold Rb gas was recently studied by the group of Dr. Lewandowski. Her group for the first time have observed the losses of molecules from the electrostatic trap which can be caused by the collisions with coolant (Rb). Estimated cross-sections from the state $|1, 1, u>$ turned out to be significantly larger than those reported in the paper **[H6]**. To explain that, we extended the theoretical model for the case of external electric field. New theoretical studies have confirmed the experimental findings, and the most important enhancement of inelastic cross-sections is due to the fact, that the initial state $|1, 1, u>$ splits into two states in the field, and additional channel appears in the system. Such channel is very strongly coupled to the initial state, hence the strongly inelastic character of the collisions. Also, in the presence of electric field the J quantum number is no longer conserved and the electric field strongly mixes the states with different L quantum number again, causing strong, additional couplings in the system. Theoretical predictions are very sensitive on

details of the potential, hence, we were not able to predict quantitatively any scattering properties. However, it was possible to demonstrate the effect of electric field on the inelastic cross-sections, for any modification of the interaction potential. The common publication with the group of H. Lewandowski appeared in 2011 in Physical Review Letters [**P1**].

- **Theoretical and experimental studies of isotope effect in Penning ionization in the system He*+hydrogen.**
  Results of the paper [**H8**] were of extreme relevance for the experimental group of prof. Nareviciusa (Weizmann Institute, Israel). A modification of the isotropic part of the potential (by scaling) for the He^*+H_2 system followed by scattering calculations have suggested that plausible values of scaling factor that give the exact positions of shape resonances (for collision energies 1 meV–100 meV) are 0.75 and 1.15. This ambiguity is removed once the data of the cross-sections for He^*+D_2 and He^*+HD collisions were available. It turns out, that the only sensible value of scaling factor of potential is 1.15 - in such case the modified potential predicts the correct positions of resonances for all three isotope combinations. Also, the 15% modification of the original potential is possible within the expected uncertainty, while the 0.75 factor is quite unlikely. The publication [**P2**], which appeared in 2014 in Nature Chemistry is the first published work in which the isotope effect on the chemical reaction could be predicted theoretically. From the point of view of theory the measurement of low-energy cross section is one of the most important tests of quality of the interaction potentials.

- **Electronic structure of diatomic molecules relevant in ultracold matter physics.**
  A significant part of my research in recent year was devoted to the electronic structure of molecules which are subject to extensive experimental study, in particular KRb, RbCs, RbYb, He*Rb, RbSr ([**P3-P6**]: one of these papers is in press, other under Phys. Rev. Lett. consideration). In particular, spectroscopic constants, energy levels and potential energy curves were the main point of these studies. In the paper [**P3**] we have studied for the first time the hyperfine energy levels of KRb and RbCs molecules in their ground states. We have used quantum chemistry methods to obtain the essential coupling constants, such as nuclear spin–spin, shielding constants, electric field gradient at nuclei. These research have turned out to be essential in designing the trapping of the KRb molecules in the optical trap, and conditions for the STIRAP transfer toward the ground state.

  The paper [**P5**] was a joint, interdisciplinary effort of the experimental group of A. Görlitz

(Dusseldorf), and few theoreticians, focused on determination of the potential energy curves and scattering lengths in the RbYb system. With extensive *ab initio* studies we have predicted the initial potentials which later were subsequently refined using the two-color photoassociation spectroscopy. The obtained RbYb potential and scattering lengths in all Rb and Yb isotopic combinations are crucial in future work on magnetic or optical Feshbach resonances. Simiarly to RbYb, the work (in collaboration with prof. Dulieu) on RbSr system was inspired by extensive experimental studies of this mixture by the group of prof. F. Schreck (first IQOQI, now Amsterdam). We have carried out the *ab initio* calculations of the potential energy curves of ground- and excited states of RbSr (the paper **[P5]** has just been accepted for the publication in Phys. Rev. A). The potentials are now used to reproduce the relevant spectroscopic measurements, and their refinement.

Recently I have started the collaboration with dr. S. Knoop (Vrije University Amsterdam) who leads the experimental research on quantum gas of metastable helium and rubidium atoms. My contribution to our collaboration is focused on calculations of accurate interaction potentials, inelastic rates and predictions of the behaviour of the Feshbach resonances. In particular, we managed for the first time to predict accurately the scattering length for the system with many electrons. First results of our collaboration has already been submitted to Physical Review Letters **[P6]**.

- **Cold molecule+molecule collisions in magnetic fields.**
  Apart from sympathetic cooling, the crucial question from the point of view of production of cold molecules is if the molecules can be evaporatively cooled, so that their phase-space density becomes large enough to achieve quantum degeneracy. In recent years I was involved in common project of groups at Durham University and Radboud University (Nijmegen, group lead by prof. Groenenboom) devoted to NH+NH molecules collisions in the magnetic field. To this end we obtained the accurate *ab initio* potential with state-of-the-art quantum chemistry methods, and afterwards, quantum scattering calculations has been performed: in presence of the magnetic field, and with no external fields. Each of these tasks was very challenging and was published separately **[P10–P12]**.

  The main result of these works was the energetic dependance of the cross-sections for spin-changing collisions. The problem was computationally very expensive and thus, we have decided to use unconverged basis set of monomers in our study. In the field-free calculations we could afford to converge the basis sets and these calculations served us as a benchmark for the magnetic field calculations. Eventually we have found that the ^{15}NH is a very promising candidate for evaporative cooling and our results does not depend

neither on the basis set used nor on the potential modification.

- **Collisions of Li with molecules**

  I was also involved in research on the interactions and collision of the lithium atoms with molecules, which were reported in the papers [**P7**–**P9**]. The Li+LiH studies were done in collaboration with the group of prof. Moszynski from Warsaw University, which performed most of state-of-the-art *ab initio* calculations for that system. The potential surface published in the paper [**P8**] is at present one of the most accurate three -atom interaction potential. The potential surface was used later to evaluate the cross-sections for Li+LiH (LiH in $j = 1$ rotational state) collisions. The cross-sections were used later to perform the simulations of sympathetic cooling of LiH by collisions with Li in the microwave and AC trap [**P9**].

  Studies of Li+NH system also complete the research on N+NH. As a matter of fact, Li+NH system should be easier to implement experimentally, since the cooling of Li atoms is state-of-the-art technique. We obtained *ab initio* potential energy surface with CCSD(T) method, with very good accuracy. The anisotropy of the potential is very large, similar to Rb+ammonia system. We found, however, that the inelastic cross-sections are not extremely large: they typically remain 100 smaller than elastic cross sections which is promising for the sympathetic cooling. Although the cross-section depend very strongly on modification of potential within estimated uncertainty, their ratio remains favourable for sympathetic cooling. The reason why, despite large anisotropy, the inelastic cross-sections remain weak, is apparently large centrifugal d-wave barrier, which suppresses the outgoing wavefunction.

5.2 Intermolecular interactions: new approaches and applications

My PhD thesis was devoted to the implementation of symmetry-adapted perturbation theory (SAPT) for the open-shell high-spin systems, which is a perturbative approach for the calculations of interaction energies in weakly-bound (Van der Waals, non-covalent) systems. After defending my thesis I continued research on Van der Waals forces, in particular I was interested in applications of density functional theory (DFT) in studies of non-covalent systems with dominant role of the dispersion, further development of SAPT method and applications of SAPT to chemically important systems.

- **Symmetry adapted perturbation theory.**

  The SAPT method implemented by me during my PhD studies was developed further, for the case of unrestricted Slater determinants as a reference states. In collaboration

with prof. Chalasinski's group we have implemented the equations more efficiently and tested the SAPT method for several unstudied before systems [**P20**], such as for example NO radical with noble-gas atoms. The application of SAPT method was crucial for the determination of interaction potentials of metastable He and Ne atoms with molecules [**H8**].

Among other successful applications of SAPT which were subject of my research were the studies of interactions in metal clusters and dimers: Cr_2 , ScCr [**P18**] i Au_2 [**P19**]. In each of these cases the crucial benefit from SAPT was the information about the dispersion interaction in the system. The metallic systems are very challenging for the quantum chemistry: the applications of complementary methods to study these systems is essential. The research revealed that for the dispersion interaction the contribution of the outermost electronic shells is the crucial. Also, the perturbation theory provided the information about the anisotropy of the interaction in the ScCr system. The system which was also interesting to me was the interaction of water and NO molecule [**P16**]: for this, particularly difficult system we were able to study the anisotropy of the interaction potential components and predict their behaviour for arbitrary geometry. It turns out, that the electrostatic interaction and exchange interactions exhibit the strongest anisotropy.

In recent years, triatomic clusters of alkali-metals and second-group atoms were also the subject of my studies. I have implemented the non-additive Heitler-London interaction energy (the first-order interaction energy) for three-body systems. In collaboration with dr. Klos (University of Maryland) and prof. Chalasinski we have applied this approach to such triatomic systems as eg. Be_3, Ca_3, Li_3, Na_3 [**P17**] from which we could learn that the main mechanism that contributes to non-additivity comes from the first-order. Using the correlated methods for the excited states we also found out, that the role of non-additive interactions is even more profound for the excited states.

- **Dispersion interactions in density functional theory.**
  In present electronic structure theory, the density functional theory plays a major role, since it is by far the most inexpensive method of calculation of the electronic energy with electron correlation. One of the major obstacle in using DFT to predict the properties of molecular systems bound with non-covalent forces (such as eg. DNA helices, water clusters) is that it fails to predict the dispersion interaction correctly. This disadvantage is due to the fact, that the DFT theory in current formulation is local. The Kohn-Sham equations, which are used to evaluate the density and electronic energy depend only on local effective potentials of electrons in the system, thus the resulting energies

do not include the long-range electron-electron correlation. This is one of the most fundamental problem in electronic structure theory and the ultimate remedy to solve it is still unknown.

In 2010, in collaboration with the group of prof. Chalasinski (Warsaw University) and prof. Szczesniak (Rochester University) we have proposed a new method for calculation of interaction energy based on DFT description in which the dispersion is exactly separated from the short-range correlation effect. To this end we have reformulated the Kohn-Sham equations for the pair of interacting monomers: for the self-consistent field equations for monomers we have added the Hartree potential and the exact exchange potential of the second monomer. In this manner it is possible to obtain the interaction energies which correctly describes intramonomer correlation and has no dispersion interaction included. The latter can be calculated perturbatively and added *a posteriori*. The method was tested for number of representative systems and demonstrated good prospects.

The result of these studies were published in three publications **[P13-P15]** one of them, in Physical Review Letters. The method has a potential for further development: for example for many-body clusters or open-shell systems.

5.3 List of publications not included in sec. 4, completed after PhD degree

[P1] L. P. Parazzoli, N. J. Fitch, P. S. Żuchowski, J. M. Hutson, H. J. Lewandowski
Large effects of electric fields on atom-molecule collisions at millikelvin temperatures
Phys. Rev. Lett. 106, 193201 (2011)

[P2] E. Lavert-Ofir, Y. Shagam, A. B. Henson, S. Gersten, J. Kłos, P. S. Żuchowski, J. Narevicius, E. Narevicius
Observation of the isotope effect in sub-kelvin reactions
Nature chemistry 6 (4), 332

[P3] J. Aldegunde, B. A. Rivington, P. S. Żuchowski, J. M. Hutson
Hyperfine energy levels of alkali-metal dimers: ground-state polar molecules in electric and magnetic fields
Phys. Rev. A, 78, 033434 (2008)

[P4] P. S. Żuchowski, R. Guerout, O. Dulieu
Ground and excited state properties of the polar and paramagnetic RbSr molecule: a comparative study
arXiv:1402.0702 (in press, Phys. Rev. A)

[P5] M. Borkowski, P. S. Żuchowski, R. Ciuryło, P. S. Julienne, D. Kędziera, L. Mentel, P. Tecmer, F. Münchow, C. Bruni, A. Görlitz
Scattering lengths in isotopologues of the RbYb system
Phys. Rev. A 88, 052708 (2013)

[P6] S. Knoop, P. S. Żuchowski, D. Kędziera, Ł. Mentel, M. Puchalski, H. P. Mishra, A. S. Flores, W. Vassen
Ultracold mixtures of metastable He and Rb: scattering lengths from ab initio calculations and thermalization measurements
arXiv:1404.4826

[P7] A. O. G. Wallis, E. J. J. Longdon, P. S. Żuchowski, J. M. Hutson
The prospects of sympathetic cooling of NH molecules with Li atoms
Eur. Phys. J. D 65, 151 (2011)

[P8] W. Skomorowski, F. Pawłowski, T. Korona, R. Moszynski, P. S. Żuchowski, J. M. Hutson
Interaction between LiH molecule and Li atom from state-of-the-art electronic structure calculations
J. Chem. Phys. 134, 114109 (2011)

[P9] S. K. Tokunaga, W. Skomorowski, P. S. Żuchowski, R. Moszynski, J. M. Hutson, E. A. Hinds, M. R. Tarbutt
Prospects for sympathetic cooling of molecules in electrostatic, ac and microwave traps
Eur. Phys. J. D 65, 141

[P10] L. M. C. Janssen, G. C. Groenenboom, A. van der Avoird, P. S. Żuchowski, R. Podeszwa
Ab initio potential energy surfaces for NH—NH with analytical long range
J. Chem. Phys. 131, 224314 (2009)

[P11] L. M. C. Janssen, P. S. Żuchowski, A. van der Avoird, G. C. Groenenboom, J. M. Hutson
Cold and ultracold NH–NH collisions in magnetic fields
Phys. Rev. A. 83, 022713 (2011)

[P12] L. M. C. Janssen, P. S. Żuchowski, A. van der Avoird, J. M. Hutson, G. C. Groenenboom
Cold and ultracold NH–NH collisions: The field-free case
Phys. Rev. A. 83, 022713 (2011)

[P13] L. Rajchel, P. S. Żuchowski, M. M. Szczesniak, G. Chałasinski
Density functional approach to Non-Covalent Interactions via Monomer Polarization and Pauli Blockade
Phys. Rev. Lett. 104, 163001 (2010)

[P14] L. Rajchel, P. S. Żuchowski, M. M. Szczesniak, G. Chałasinski
Derivation of the supermolecular interaction energy from the monomer densities in the density functional theory
Chem. Phys. Lett. 486, 160 (2010)

[P15] L. Rajchel, P. S. Żuchowski, M. Hapka, M. Modrzejewski, M. M. Szczesniak, G. Chałasinski
A density functional theory approach to noncovalent interactions via interacting monomer densities
Phys. Chem. Chem. Phys. 12, 14686 (2010)

[P16] H. Cybulski, P. S. Żuchowski, B. Fernandez, J. Sadlej
The water-nitric oxide intermolecular potential-energy surface revisited
J. Chem. Phys. 130, 104303 (2009)

[P17] J. Kłos, P. S. Żuchowski, L. Rajchel, G. Chałasiński, M. M. Szczesniak
Nonadditive interactions in ns^2 and spin-polarized ns metal atom trimers
J. Chem. Phys. 129, 134302 (2008)

[P18] L. Rajchel, P. S. Żuchowski, J. Kłos, M. M. Szczęśniak, G. Chałasiński
Interactions of transition metal atoms in high-spin states: Cr_2, Sc–Cr, and Sc–Kr
J. Chem. Phys. 127, 244302 (2007)

[P19] R.-F. Liu, C. A. Franzese, R. Malek, P. S. Żuchowski, J. G. Angyan, M. M. Szczęśniak, G. Chałasiński
Aurophilic Interactions from Wave Function, Symmetry-Adapted Perturbation Theory, and Rangehybrid Approaches
J. Chem. Theory Comput. 8, 2399 (2011)

[P20] M. Hapka, P. S. Żuchowski, M. M. Szczęśniak, G. Chałasiński
Symmetry-adapted perturbation theory based on unrestricted Kohn-Sham orbitals for high-spin open-shell van der Waals complexes
J. Chem. Phys. 137, 164104 (2012)

5.4 Bibliometric data

- H-index: 14
- number of citations: 490
- number of papers published: 33 (1 in press, 1 submitted)

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