Charles University, Faculty of Mathematics and Physics
Institute of Theoretical Physics

# Resonant collisions of electrons and anions with molecules: from diatomics to polyatomics

habilitation thesis

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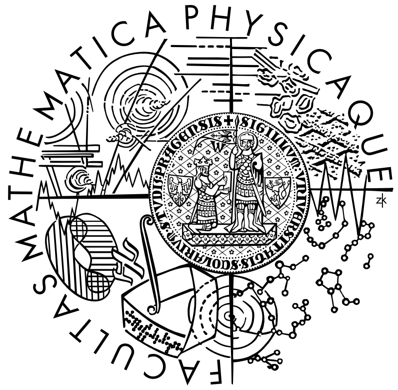

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## Acknowledgement

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# Introduction

This habilitation thesis is a summary of the original results, on which I have significantly participated and which were published in scientific journals. They were obtained mainly during my work at the Institute of Theoretical Physics of the Faculty of Mathematics and Physics, Charles University in Prague and partially also during my two-year stay as a postdoc at the Lawrence Berkeley National Laboratory in the USA.

The published papers cover the topics which are related to resonant collisions of electrons with molecules at low energies and collisions of anions with atoms and molecules. In my work I focused mainly on models for nuclear dynamics of these processes and on the detailed interpretation of the cross sections, especially for vibrational excitation of a molecule by the electron impact. Critical evaluation of the approximations and testing of numerical methods, which are commonly used to solve equations describing nuclear dynamics, is also important part of my research.

I divided the publications included in this thesis into three topics which are briefly described here and in detail in the following chapter. The cited papers are reprinted in the chapter Original papers.

- *Two-dimensional model for diatomic molecules*
  The first topic (see the section 1.1) includes my work on a simple two-dimensional model for electron collisions with diatomic molecules with one electronic and one nuclear degree of freedom introduced in [1]. This model enabled us to probe approximate methods for nuclear dynamics of these collisions and to evaluate applicability of these methods for various systems [1, 2]. Time-dependent solution of this model provided a useful tool for interpretation of the vibrational excitation cross sections [3]. Recently this model was modified to a case of electron collisions with molecular cation $H_2^+$ to probe approximate methods describing indirect mechanism of dissociative recombination [4].

- *Diatomic molecules: interpretation of the cross sections*
  Into this topic (see the section 1.2) I chose the papers on which I participated and which focused on electron collisions with specific diatomic molecules such as $H_2$ [5, 6], NO [7], DI [8] or HCl [9], and also on the interpretation of energy-dependence of the cross sections, especially of the oscillatory structure in the vibrational excitation cross sections [10, 11]. As an important contribution in this topic I consider a simple explanation of these structures for $e^- + H_2$ system in [6], the origin of which was for many years unclear, and also an explanation of asymmetric peaks appearing in these structures in [10, 3].

- *Towards polyatomic molecules*
  Finally, the last topic (see the section 1.3) includes our recent work focusing on systems with more than one nuclear degree of freedom, such as electron collisions with polyatomic molecules [12] and closely related collisions of negative atomic ions with molecules [13,

14, 15]. These papers contain our first attempts to deal with the dynamics of negative polyatomic molecular ions.

Apart from these papers I also published, in collaboration with my students and colleagues, several other papers which were not included in this thesis to keep it compact and focused on selected topics. One of important steps towards calculation of the cross sections is numerical solution of the effective equations for nuclear motion, therefore we tested several numerical techniques for solving these equations [16, 17, 18]. Another work which resulted in several papers with my student Jakub Benda [19, 20, 21, 22, 23] was inspired by our colleagues from the Astronomical institute of the Academy of Sciences who needed reliable scattering data for many processes occurring in electron collisions with hydrogen atoms, such as electronic excitation and ionization. Under my supervision Jakub Benda wrote several codes to calculate these data and critically compared his results with experimental and theoretical data in the literature and databases. The scattering data obtained within this project are available for the scientific community from the website http://utf.mff.cuni.cz/data/hex/.

Finally let me mention my work on the Perl scripts published as a CCPforge project UKRmol-scripts in the United Kingdom [24]. These scripts enabled the users to set up in an easy way fixed-nuclei electron-molecule scattering calculations within the UKRmol suite of codes [25, 26, 27] and to run these calculations for many geometries straightforwardly without preparing manually many input files. These scripts were later modified by my former student Zdeněk Mašín for calculations of photoionization of molecules and applied to $NO_2$ [28].

# Contents

# Chapter 1

# Overview of studied problems

Before I describe the particular topics I worked on, let me first write a few paragraphs on resonant electron-molecule collisions and related collisions of anions with atoms or molecules in general to explain why these topics are interesting from a theoretical point of view and why I focused in my research on the selected topics.

Experiments on electron-molecule collisions performed by Schultz in 1960's (see his review [29] and references therein) and improved later by other experimental groups (to mentions a few, Allan's group in Fribourg, Switzerland, Hotop's group in Heidelberg, Germany, Buckman's group in Canberra, Australia, see for example reviews by Brunger and Buckman [30], and Allan [31]) inspired theoreticians over the years and lead to developments in the description of both fixed-nuclei electron scattering calculations and the nuclear dynamics of these processes. Low-energy resonant electron collisions with molecules, during which an intermediate negative molecular ion is formed in a temporary state, attracted molecular physicists primarily because of richness of structures appearing in the cross sections, especially in such processes as vibrational excitation (VE) of molecules due to electron impact

$$\mathrm{e}^- + \mathrm{X}(\nu_i) \to \mathrm{X}^- \to \mathrm{e} + \mathrm{X}(\nu_f)\,, \tag{1.1}$$

dissociative electron attachment (DA)

$$\mathrm{e}^- + \mathrm{X} \to \mathrm{X}^- \to \mathrm{Y} + \mathrm{Z}^- \tag{1.2}$$

and inverse process of associative detachment (AD)

$$\mathrm{Y} + \mathrm{Z}^- \to \mathrm{X}^- \to \mathrm{e}^- + \mathrm{X}\,, \tag{1.3}$$

where X stands for a molecule and Y and Z are parts (an atom or a molecule) of the molecule X. An example of the process with a diatomic molecule is $e^- + HCl \to H + Cl^-$ and of the process with a triatomic molecule $O^- + H_2 \to e^- + H_2O$. The structures observed in the cross sections such as pronounced threshold peaks (the first evidence for hydrogen halides and $H_2O$ was provided by [32] and [33], see also [34] and references therein), Wigner cusps (see e.g. [35, 36]) or oscillations below the DA threshold in the VE cross sections (for the first time observed experimentally in the system $e^- + N_2$ at energies around 2.3 eV [37]) demanded explanations.

Another reason for studying these basic molecular processes is their importance in many fields of physics [38]. Reliable data are needed, for example, to determine the composition of planetary or stellar atmospheres, interstellar clouds or the early universe and accurate knowledge of the reaction rates for these processes is important in modeling of low-temperature plasma in space and in laboratory. Despite large advances in both experimental and theoretical techniques during last several decades there are still many processes, especially those involving polyatomic molecules, for which data are still not available.

Theoretical description of the resonant processes (1.1), (1.2) and (1.3) usually consists of two steps. The first step is to perform fixed-nuclei electronic calculations for relevant geometries to determine potential energy curves/surfaces and positions and widths of resonances which are usually obtained by fitting the electron scattering eigenphase sums. The second step is a suitable model for nuclear dynamics, solution of the corresponding effective equations and calculation of the cross sections and rate coefficients.

The fixed-nuclei electronic calculations comprise the quantum chemical calculations of the potential energy curves/surfaces for both the neutral molecule, X in (1.1), (1.2) and (1.3), and the negative ion, $X^-$, and also the fixed-nuclei electron scattering calculations. Although computational chemistry achieved enormous progress in the last decades and calculation of properties of even small polyatomic molecules became more or less a routine task (though these calculations are often very time-consuming), the scattering calculations involving electron continuum are still very challenging, especially for polyatomic molecules. There are several methods which were developed for fixed-nuclei electron scattering calculations [39, 40]. Let me mention at least those which are currently actively used: the $R$-matrix approach [41] as implemented in the UKRmol package [25], the complex Kohn variational principle [42], the Schwinger variational principle [43, 44], and the single center expansion approach [45].

Among the earliest theoretical works on the nuclear dynamics of resonant electron-molecule collisions were that of O'Malley [46, 47] and O'Malley and Taylor [48] on dissociative attachment based on the idea of Feshbach partitioning [49] of the electron scattering wave function into a resonant and nonresonant part. Herzenberg *et al* [50, 51, 52] later applied these ideas to vibrational excitation and developed the local complex potential (LCP) approximation that is also known as the boomerang model in this context. More sophisticated approaches involving nonlocal, complex and energy-dependent potentials for nuclear motion have been developed since then [53, 54], and applied to a number of diatomic systems. The class of such methods based on projection operators, which is called the nonlocal resonance model (NRM), was reviewed by Domcke [55] and by Čížek and Houfek [56]. There were also other approaches developed simultaneously but I will not attempt to go into details of these methods, see e.g. reviews by Morrison [57], Fabrikant [58] and the books [38, 39].

The nonlocal resonance model was successfully used to study electron collisions with many diatomic molecules. In our group we have concentrated on development of numerical methods to solve the nuclear dynamics within this model and we performed calculations for several systems, especially for hydrogen molecule and hydrogen halides (see Houfek and Čížek [59] and references therein for a summary of results). I participated on several such studies and I focused mainly on the interpretation of the features appearing in the VE cross sections. The main results are summarized in the section 1.2.

Although the calculated cross sections were usually in good agreement with available experiments, there was no direct study of the validity of various approaches to nuclear dynamics because it is still impossible to solve the full problem even for the smallest $H_2$ molecule. Therefore, we proposed a simple two-dimensional model of resonant electron-molecule collisions [1] which can be solved numerically exactly without having to resort to the Born-Oppenheimer approximation and which can be used for testing these approximate approaches. The 2D model and results of benchmark studies based on it are summarized in the section 1.1.

At present, for several diatomic systems, not only qualitative but also quantitative consensus has been reached between theory and experiment. That is not the case when polyatomic molecules are concerned. Only the nuclear dynamics in one or two nuclear degrees of freedom were often considered, see e.g. [60, 61] for the $CO_2$ molecule, because of both computational demands and difficulties with construction of models in more dimensions. For example, the potential energy surfaces of polyatomic molecules in three dimensions can have peculiar shapes including occurrence of conical intersections [62] which make the situation much more complicated than for diatomic molecules. First studies of the dynamics of electron interactions with polyatomic molecules involving all nuclear degrees of freedom were accomplished for carbon dioxide [63, 64, 65] and water [66, 67]. Calculations were performed within the local complex potential approximation using the multi-configuration time-dependent Hartree (MCTDH) method [68]. My first encounter with multidimensional dynamics was the work on the $e^- + CF_3Cl$ system [12] but we used also the LCP approximation and moreover only two nuclear degrees of freedom and only one of them was dissociative. As far as I know the only attempt to do multidimensional nuclear dynamics within nonlocal theory was done by Kazansky [69] but within a model with two degrees of freedom. Therefore, we decided to start a comprehensive study of the lowest-lying states of the water anion $H_2O^-$ where application of the nonlocal theory is necessary for the LCP approximation fails because there is no resonance corresponding to the lowest ${}^2A_1$ state of $H_2O^-$. Examples of our results for this system are shown in the section 1.3. Currently we work on the construction of the full nonlocal resonance model for this system.

## 1.1 Two-dimensional model for diatomic molecules

As mentioned above, the nuclear dynamics of resonance collisions of electrons with molecules is most often described either by the local complex potential (LCP) approximation or within a more general nonlocal theory by the so-called nonlocal resonance model (NRM). The validity of these approaches is usually verified afterwards by agreement or disagreement of the calculated cross sections with experimental results. Even for the simplest system $e^- + H_2$ it is not possible to verify their validity directly by comparing them with exact calculations. For this reason, we proposed a two-dimensional model with one nuclear and one electron degree of freedom, which would include all the basic characteristics of resonant low-energy collisions of electrons with diatomic molecules and which can be solved numerically exactly without any physical approximations.

A detailed description of the two-dimensional model and its numerical solution using the finite-element method combined with discrete variable representation and exterior complex scaling method for taking care of outgoing boundary conditions is given in [1] where the model was introduced for the first time. Here I will only give basic description of the 2D model and the local and nonlocal approximations applied to it.

If a model Hamiltonian is to capture the fundamental dynamics of resonance collisions of electrons with diatomic molecules in which nuclear motion plays a significant role, it must have at least two degrees of freedom, the first corresponding to the incoming electron and the other to vibrational and eventually dissociative motion of the nuclei. The electronic coordinate $r$ will describe the distance of the electron from the molecule and the nuclear coordinate $R$ corresponds to the internuclear distance in the diatomic molecule. Since it is a model system,

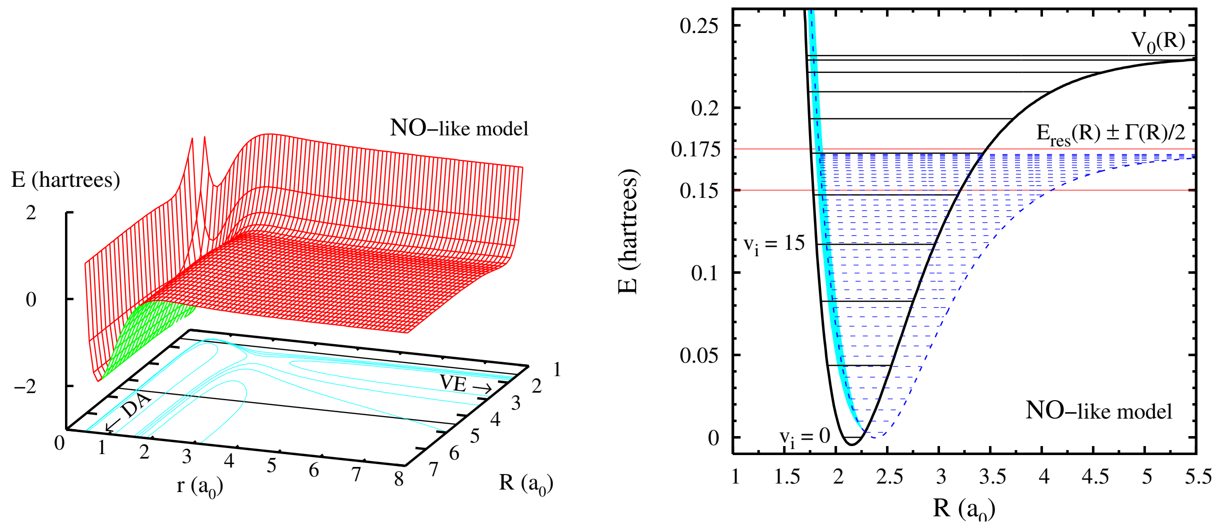

Figure 1.1: The full two-dimensional potential $V_0(R) + l(l+1)/2r^2 + V_{\mathrm{int}}(R,r)$ for the NO-like model (left panel) and the corresponding potentials for nuclear motion from fixed-nuclei calculations. Internuclear distances are given in units of Bohr radius $a_0 = 5.291772 \times 10^{-11}$ m.

there is no point in asking whether the distance $r$ is considered from the center of the molecule or from one of the nuclei. It is only important whether the interaction between the nuclear and electronic degrees of freedom accounts for the resonant behavior of the system $\mathrm{e}^- + \mathrm{X}$. The simplest such Hamiltonian can be written as

$$H = -\frac{1}{2\mu}\frac{d^2}{dR^2} + V_0(R) - \frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{\mathrm{int}}(R,r)\,, \tag{1.4}$$

where the first two terms describe the vibrational motion of the diatomic molecule with the reduced mass $\mu$, the next two terms correspond to an electron incoming with a certain angular momentum $l$ depending on the system that we model. The last term $V_{\mathrm{int}}(R,r)$ is a suitable interaction potential chosen in such a way to get a specific behavior of some real system. In the papers [1, 2] we introduces three such models: the NO-like and $\mathrm{F}_2$-like models with $l = 1$ ($p$-wave resonances) and the $\mathrm{N}_2$-like model with $l = 2$ (a $d$-wave resonance). As an illustration the full 2D potential and corresponding one-dimensional potentials for nuclear motion obtained from fixed-nuclei calculations which will be explained below, are shown in Figure 1.1 for the NO-like model.

Below I only briefly describe a time-independent scattering solution of the 2D model with initial conditions corresponding to the vibrational excitation process [1], for the time-dependent approach to the same problem see [3]. We are interested in the scattering solution where the molecule is initially in a certain vibrational state $\chi_{v_\mathrm{i}}(R)$, a bound state of $V_0(R)$, and the electron is initially in a continuum state described by an energy-normalized wave function $\mathcal{J}^l_{k_\mathrm{i}}(r) = \sqrt{\frac{2k_\mathrm{i}}{\pi}}\, r j_l(k_\mathrm{i} r)$ where $k_\mathrm{i}$ denotes momentum of the incoming electron with energy $E_\mathrm{i} = k_\mathrm{i}^2/2$ and $j_l$ is a spherical Bessel function [70]. A scattering solution with the total energy $E = E_{v_\mathrm{i}} + E_\mathrm{i}$ can then be expressed as

$$|\Psi^+\rangle = |\chi_{v_\mathrm{i}}\mathcal{J}^l_{k_\mathrm{i}}\rangle + \frac{1}{E - H + i\eta} V_{\mathrm{int}} |\chi_{v_\mathrm{i}}\mathcal{J}^l_{k_\mathrm{i}}\rangle\,, \tag{1.5}$$

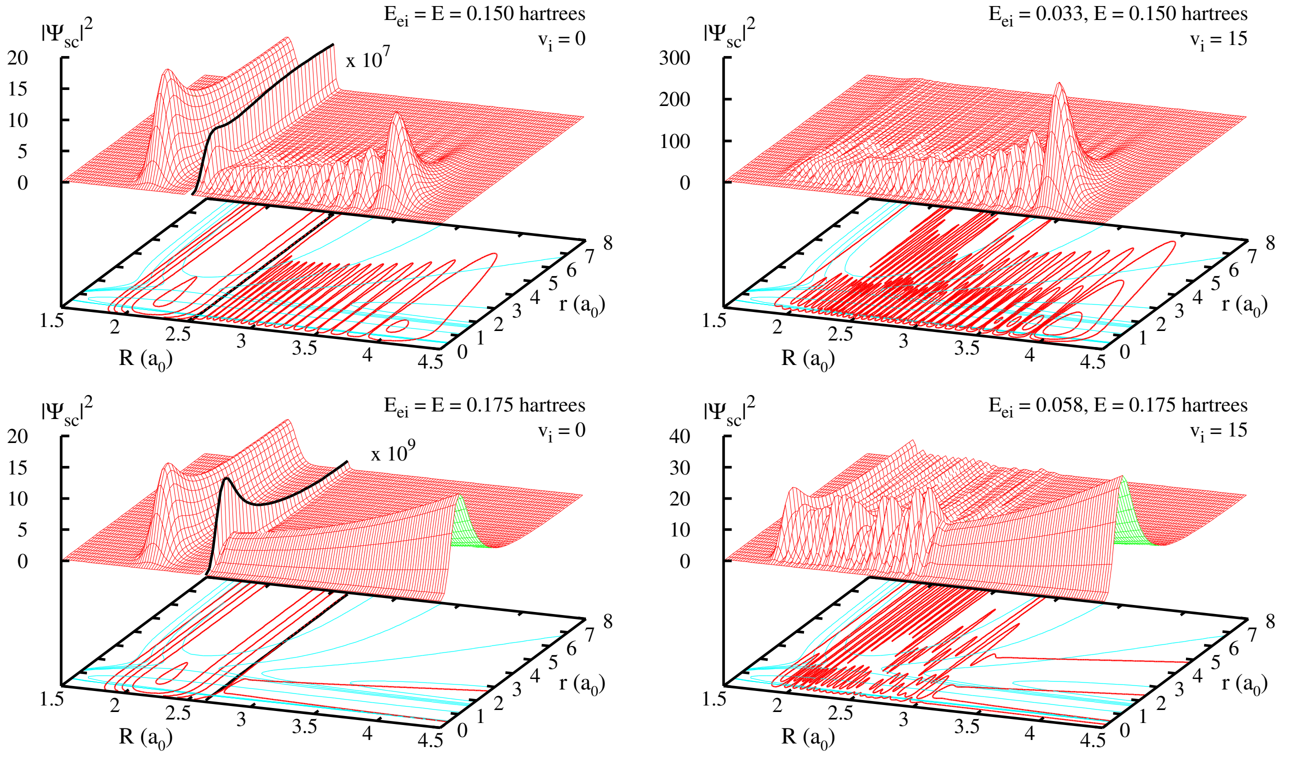

Figure 1.2: Squared modulus of scattered part of the wave functions $\Psi^{+}(R,r)$ for the NO-like model for two initial vibrational states ($v_{\mathrm{i}} = 0$ and 15) at total energies of $E = 0.150$ and 0.175 hartrees (also marked in Figure 1.1, right panel). The wave functions for initial state $v_{\mathrm{i}} = 0$ were magnified by $10^7$ at $E = 0.15$ hartrees and $10^9$ at $E = 0.175$ hartrees for $R > 2.5$ a$_0$ (beyond the dark line).

where the first term on the right-hand side describes the initial state of the model system and the second term is a scattered wave. An illustration of the scattered waves for the NO-like model for two energies showed as red lines in Figure 1.1, right panel, and for two initial vibrational states is in Figure 1.2. The upper panels show a case when the DA channel is closed (the wave function is confined in the nuclear coordinate $R$) and the lower panels show a case when it is open (there is an outgoing wave for large $R$). Nice animations illustrating what happens during collisions in the time-dependent picture were provided as Supplemental Material to our paper [3].

From $|\Psi^{+}\rangle$ we can determine $T$ matrices for vibrational excitation and dissociative electron attachment as

$$
\begin{aligned}
T^{\mathrm{VE}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}}(E) &= \langle \chi_{v_{\mathrm{f}}} \mathcal{J}^{l}_{k_{\mathrm{f}}} | V_{\mathrm{int}} | \Psi^{+} \rangle \,, && (1.6)\\
T^{\mathrm{DA}}_{v_{\mathrm{i}}}(E) &= \langle \mathcal{E}_{K_{\mathrm{DA}}} \phi_{\mathrm{b}} | V_0 + V_{\mathrm{int}} - V_{\mathrm{b}} | \Psi^{+} \rangle && (1.7)
\end{aligned}
$$

where $\chi_{v_{\mathrm{f}}}$ is a final vibrational states of the molecule, $\mathcal{J}^{l}_{k_{\mathrm{f}}}(r)$ corresponds to an outgoing electron, $\mathcal{E}_K(R) = \sqrt{\frac{2\mu}{\pi K}}\sin(KR)$ describes relative motion of the nuclei with momentum $K_{\mathrm{DA}}$ if the dissociative attachment channel is open, and $\phi_{\mathrm{b}}(r)$ is the electronic bound state in this channel, which is a solution of the equation

$$\left(T_r + \frac{l(l+1)}{2r^2} + V_{\mathrm{b}}(r)\right)\phi_{\mathrm{b}}(r) = -E_a\phi_{\mathrm{b}}(r)\,, \tag{1.8}$$

where $V_{\mathrm{b}}(r)$ is the limit of the interaction potential for large internuclear distances and $E_a$ is the electron affinity of the atom to which the electron is attached in a modeled real system. From the $T$ matrices we can compute the cross sections for the processes we are interested in as

$$\sigma^{\mathrm{VE}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}}(E) = \frac{4\pi^3}{k_{\mathrm{i}}^2}\left|T^{\mathrm{VE}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}}(E)\right|^2, \tag{1.9}$$

$$\sigma^{\mathrm{DA}}_{v_{\mathrm{i}}}(E) = \frac{4\pi^3}{k_{\mathrm{i}}^2}\left|T^{\mathrm{DA}}_{v_{\mathrm{i}}}(E)\right|^2 \tag{1.10}$$

where coefficients correspond to the energy-normalized electron scattering states.

The basic assumption of the nonlocal theory of nuclear dynamics of electron-molecule collisions is formation of the temporary molecular ion X$^-$ where the electron is captured into a resonant state which is approximately described by a normalized square integrable function $\phi_d(r;R)$ which is called a discrete state in this context and which should be slightly dependent on the internuclear distance compared to dependence of the corresponding nuclear wave function $\Psi^+_{\mathrm{d}}(R)$. To derive effective equations for nuclear dynamics within the nonlocal theory the formalism of projection operators, which was developed by Feshbach [49, 71] for nuclear reactions, is usually used. These operators project on the *resonant*, given by $\phi_d(r;R)$, and *non-resonant* part of the electronic Hilbert space. The latter consists of continuum functions ($\phi^+_k(r;R)$ or $\phi^-_k(r;R)$ depending on the boundary conditions) orthogonalized on the discrete state. Application of this formalism to the two-dimensional model can be found in [2]. The resulting effective equation for nuclear motion can be written as

$$\left(E + \frac{1}{2\mu}\frac{d^2}{dR^2} - V_{\mathrm{d}}(R)\right)\Psi^+_{\mathrm{d}}(R) - \int dR' F(E,R,R')\Psi^+_{\mathrm{d}}(R') = V^+_{\mathrm{d}k_{\mathrm{i}}}(R)\chi_{v_{\mathrm{i}}}(R) \tag{1.11}$$

with the nonlocal, complex and energy-dependent potential

$$F(E,R,R') = \int dR' \int k\,dk\, V^+_{\mathrm{d}k}(R)\left(E + \frac{1}{2\mu}\frac{d^2}{dR^2} - V_0 - k^2/2 + i\eta\right)^{-1} V^+_{\mathrm{d}k}(R')^*\,, \tag{1.12}$$

where $V_{\mathrm{d}}(R) = V_0(R) + \langle\phi_{\mathrm{d}}|H_{\mathrm{el}}|\phi_{\mathrm{d}}\rangle$ is the discrete-state potential and $V^+_{\mathrm{d}k}(R) = \langle\phi_{\mathrm{d}}|H_{\mathrm{el}}|\phi^+_k\rangle$ is the discrete-state-continuum coupling which are expressed as matrix elements of the electronic Hamiltonian

$$H_{\mathrm{el}} = T_r + \frac{l(l+1)}{2r^2} + V_{\mathrm{int}}(R,r)\,. \tag{1.13}$$

Knowledge of $V_{\mathrm{d}}(R)$ and $V^+_{\mathrm{d}k}(R)$ together with the potential of the neutral molecule $V_0(R)$ is sufficient to define the nonlocal resonance models. For the 2D model they can be computed exactly by choosing a particular discrete state but for real systems they are usually assumed to be certain functions of energy and internuclear distance and free parameters of these functions are fitted to scattering data from fixed-nuclei calculations.

The $T$ matrix for vibrational excitation within the nonlocal theory consists from two terms, a resonant and background contributions,

$$T^{\mathrm{VE}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}} = T^{\mathrm{res}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}} + T^{\mathrm{bg}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}}\,, \qquad T^{\mathrm{res}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}} = \langle\chi_{v_{\mathrm{f}}}|V^{-}_{\mathrm{d}k_{\mathrm{f}}}{}^*|\Psi^+_{\mathrm{d}}\rangle\,, \tag{1.14}$$

where $V^{-}_{\mathrm{d}k}(R) = \langle\phi_{\mathrm{d}}|H_{\mathrm{el}}|\phi^{-}_{k}\rangle$. The background term can be also expressed and calculated explicitly within the 2D model [2] but for real systems only the resonant contribution is usually considered and computed. We should note here that the expression for the resonant contribution differs from the result of Domcke in [55], Eq. (4.14), which is not general but it is valid only for the real discrete-state-continuum coupling, see [2] for explanation. The VE cross sections is evaluated in the same way as in (1.9) but the DA cross section is obtained via

$$\sigma^{\mathrm{DA}}_{v_{\mathrm{i}}}(E) = \frac{2\pi^2}{k_{\mathrm{i}}^2}\frac{K_{\mathrm{DA}}}{\mu}\lim_{R\to\infty}\left|\Psi^{+}_{\mathrm{d}}(R)\right|^2 , \tag{1.15}$$

which is equivalent to the formula (1.10) apart from the Born-Oppenheimer approximations made in the process of deriving of (1.11), see the appendix of [2].

The local complex potential approximation of (1.11) can be written as

$$\left(E + \frac{1}{2\mu}\frac{d^2}{dR^2} - V_{\mathrm{res}}(R)\right)\Psi^{LCP}_{\mathrm{d}}(R) = \zeta_{v_{\mathrm{i}}}(R)\chi_{v_{\mathrm{i}}}(R)\,, \tag{1.16}$$

where $\zeta_{v_{\mathrm{i}}}(R)$ is the so-called *entry amplitude* for capture of the electron into the resonant state which is usually approximated as $\zeta_{v_{\mathrm{i}}}(R) = \sqrt{\Gamma(R)/2\pi}$. $V_{\mathrm{res}}(R)$ is the complex potential energy of the molecular anion defined via the poles of the fixed-nuclei scattering $S$ matrix which can be obtained by finding bound or resonance energies of the electronic Hamiltonian (1.13)

$$H_{\mathrm{el}}(R)\varphi(r;R) = V_{\mathrm{res}}(R)\,\varphi(r;R)\,, \qquad V_{\mathrm{res}}(R) = E_{\mathrm{res}}(R) - \frac{i}{2}\Gamma(R)\,, \tag{1.17}$$

with all quantities depending parametrically on the internuclear distance $R$. Typically there is one bound electronic state of the molecular anion for large $R$, where $V_{\mathrm{res}}(R)$ is real and less than $V_0(R)$. That bound state becomes a resonance state at internuclear distances shorter than some critical distance, $R_c$, where the molecular anion potential energy curve crosses the potential energy curve $V_0(R)$ of the neutral molecule. For $R < R_c$ the anion potential $V_{\mathrm{res}}(R)$ is complex and the real part $E_{\mathrm{res}}(R) > V_0(R)$. See Figure 1.1, right panel, where $V_{\mathrm{res}}(R)$ is plotted together with $V_0(R)$ for the NO-like model. The VE cross sections is obtained as

$$\sigma^{\mathrm{VE}}_{v_{\mathrm{i}}\to v_{\mathrm{f}}}(E) = \frac{4\pi^3}{k_{\mathrm{ei}}^2}\left|\int_0^\infty dR\,\chi_{v_{\mathrm{f}}}(R)\zeta_{v_{\mathrm{f}}}(R)\xi_E(R)\right|^2 \tag{1.18}$$

where $\zeta_{v_{\mathrm{f}}}(R)$ is the so-called *exit amplitude* and it is also approximated as $\zeta_{v_{\mathrm{f}}}(R) = \sqrt{\Gamma(R)/2\pi}$. The DA cross section is again given by (1.15).

An example of comparison of the exact cross sections with the cross sections obtained using the nonlocal theory with the discrete state $\phi_d(r;R)$ chosen to be the bound state of the electron as $R \to \infty$ for all internuclear distances, i.e. independent of $R$, and using the LCP approximation is shown for all three studied models in Figure 1.3. We can see that the nonlocal theory works perfectly except for the vibrational excitation in the $\mathrm{F}_2$-like model for which we have to add the background contribution to get the correct cross section. On the other hand the LCP approximation, which is used much more often for real systems than the nonlocal theory for its simplicity, fails to reproduce all the cross sections. In [2] it is shown that the agreement of the nonlocal theory with the exact results for the $\mathrm{F}_2$-like model can be improved by carefully choosing the discrete state to be much more compact than it is the wave function describing the resonant state of the negative molecular ion and the background contribution can be practically eliminated.

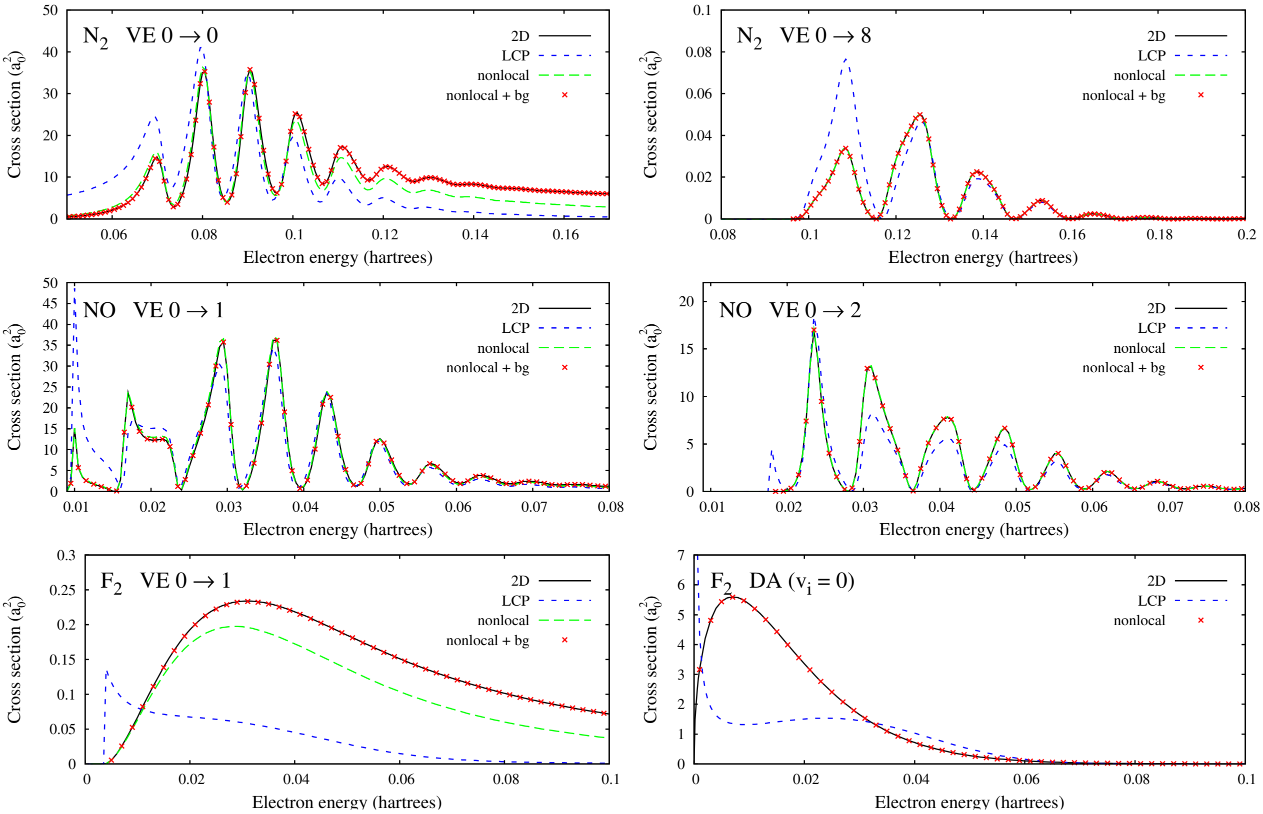

Figure 1.3: Comparison of the exact cross sections for various processes for all models introduced in [1] and [2] with results obtained within the LCP approximation and within nonlocal theory for the discrete state chosen to be the bound state of the electron as $R \to \infty$ for all internuclear distances, i.e. independent of $R$.

The 2D model for electron-molecule collisions was recently modified for the case of electron collisions with the positive molecular ion, namely with the $H_2^+$ cation, by adding the Coulomb field for the incoming electron and by changing the interaction potential to simulate the indirect mechanism for the dissociative recombination process [4]. We used this model to test validity of calculations based on a combination of multichannel quantum defect theory and frame transformation into a basis of Siegert pseudostates. Although the approximate results agree rather well with the exact ones there are still some discrepancies and the energy-dependent quantum defects will be necessary to obtain better agreement.

## 1.2 Diatomic molecules: interpretation of the cross sections

Apart from the two-dimensional model of electron-molecule collisions described in the previous section I participated on investigation of several real systems. My contribution lies mainly in the discussion of origin of various features appearing in the energy dependence of the cross sections. Therefore in the following paragraphs I focus mostly on discussion and explanation of some of these features and I will not summarize the nonlocal theory used in our calculations. It is very similar to the nonlocal theory of the 2D model described above and leads to an effective equation for nuclear dynamics with nonlocal, complex and energy-dependent potential as in the equation (1.11). A reader is referred to reviews by Domcke [55] and by Čížek and Houfek [56] for more details.

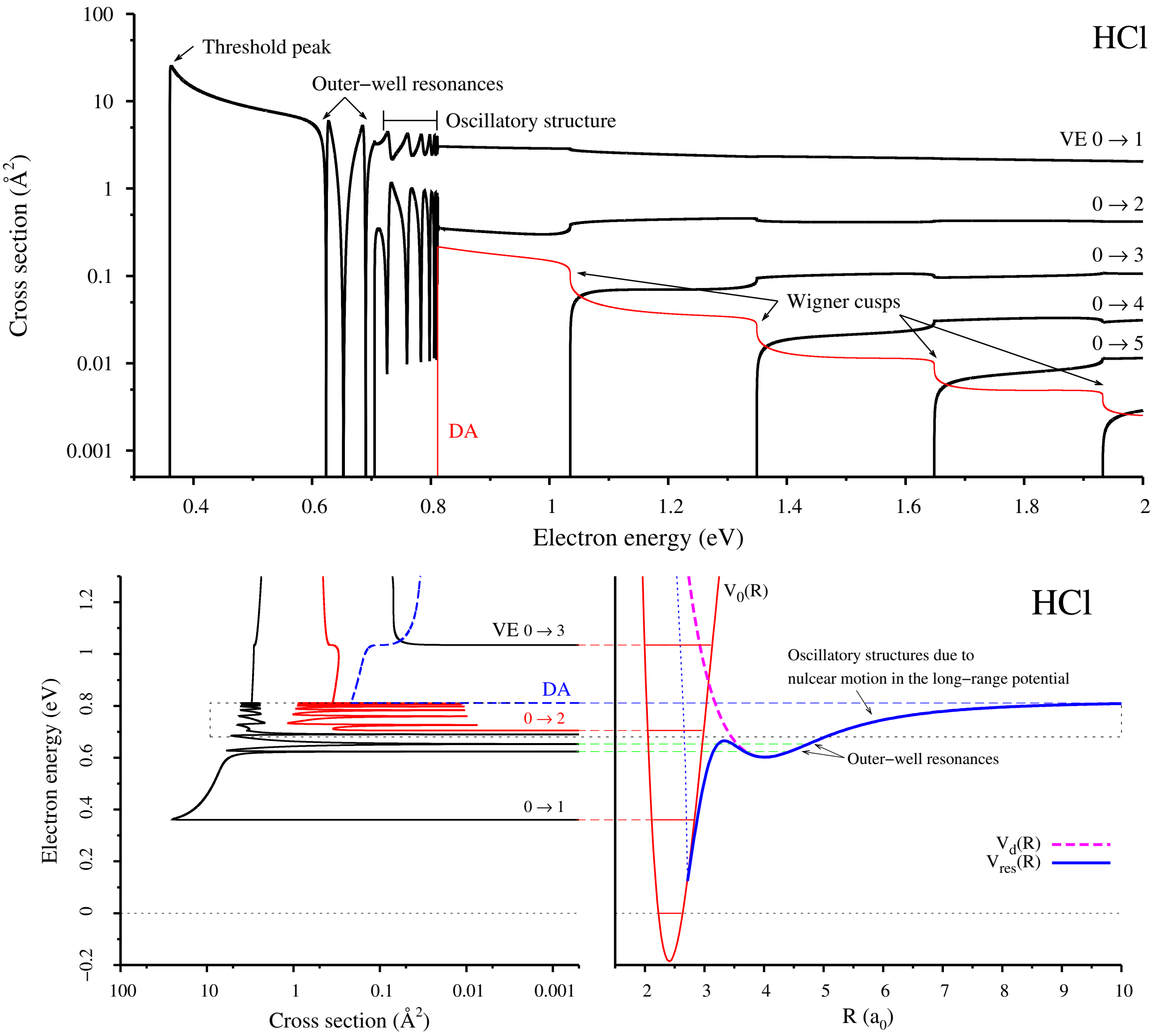

Figure 1.4: The calculated integral cross section of vibrational excitation (black lines) and dissociative attachment (red line) for the molecule HCl (upper panel). In the lower panel the same rotated cross sections are shown next to the potential energy curves of the nonlocal resonance model [9] (right panel). We can see that the origin of various features appearing in the cross sections has clear connection to the shape of the potential energy curves of the system.

To illustrate the richness of the structures in the VE and DA cross sections a collection of the cross sections for the molecule HCl in the initial ground state as calculated using the latest nonlocal resonance model of [9] is shown in Figure 1.4, upper panel. Pronounced threshold peaks and a sharp onset at thresholds often appear in the VE and DA cross sections for polar molecules such as HCl. The Wigner cusps appear in the DA cross sections at the openings of higher VE channels and oscillatory structures and narrow, outer well resonances appearing below the DA threshold in the VE cross sections result from a shape of the long-range part of the negative molecular ion potential-energy curve which governs, together with the complicated, short-range nonlocal potential, the nuclear dynamics of the system. The basic interpretation of these structures can be provided by comparison of the positions of the structures and shapes of the potential energy curves of the system as it is shown in Figure 1.4, lower panel. Another example for the HF molecule is given in Figure 3 of [11]. Comparison of the calculated cross sections with experimental results can be also found in [9] and in [11].

The oscillatory structure below the DA threshold appears in the VE cross section for all systems I work on ($H_2$ [5, 6], NO [7], DI [8] or HCl [9]). Although its origin is in general qualitatively explained by the so-called boomerang model [72, 73], for the $H_2$ molecule this explanation was disputed [74] which lead to unnecessarily complicated attempts to explain these structures by other mechanisms [75, 76]. In [6] we provided clear evidence that the oscillatory structure in the VE cross section for the $H_2$ molecule is actually a nearly perfect example of the boomerang oscillations and no further explanation of their origin is necessary. We explained that one of basic characteristics of boomerang oscillations is that the absolute magnitude of the oscillations near the DA threshold is almost the same in the VE cross sections from a given initial vibrational state $v_i$ to different final states $v_f$, but is rapidly growing when the vibrational or rotational quantum number $v_i$ of the initial state is increasing. The former behavior is illustrated in Figure 1.5, where the VE cross sections $\nu_i = 0 \to \nu_f = 0–6$ for energies near the DA threshold are shown. The latter effect was also observed for the NO molecule [7]. We can explain them if we realize that the magnitude of the oscillations is proportional to the amplitude of the reflected wave and that this amplitude depends strongly on the initial vibrational state, but not at all on the final one. The kinetic energy of the nuclear motion of the molecule in a higher initial vibrational state is larger and consequently it is more probable for the molecular anion to leave the autodetachment region before it releases an electron. The amplitude of the reflected wave will therefore be larger relative to the amplitude of the directly decaying wave. Other properties of the oscillations are described in [6].

Another problem which was not satisfactorily explained was the origin of asymmetrical peaks appearing clearly in the VE cross sections for HCl (see Figure 1.4), NO (see e.g. Figure 1.3, middle panel) and DI [8] but they can be observed also in other cases, especially for transitions to higher vibrational levels (for an example, see Figure 1.3, upper right panel, where the VE cross section for the transition 0 → 8 is plotted for the $N_2$-like model). We explained these irregular structures first within the time-independent picture in [10] by pointing out that these irregularities are caused by a combination of two phenomena: enhancing of the magnitude of the nuclear wave function in the vicinity of poles in the complex energy plane corresponding to quasi-bound vibrational states of the molecular anion, and energy variations of the phase of the nuclear wave function which corresponds to the reflection in the potential well of the molecular anion (which are actually boomerang oscillations). Later we confirmed this picture using the time-dependent solution of the 2D model in [3] where we evaluated the VE cross sections after each vibrational period of the nuclear motion. Irregularities in the oscillatory structure clearly appear after several vibrational motion of the negative molecular ion and they are caused mainly by the presence of long-lived quasi-bound vibrational states of the molecular anion.

A reader interested in these features can found their detailed explanation in [11] and [59]. Here I would like only stress our conclusion stated in [3] that all details of these structures, especially asymmetrical peaks, can be understood as quantum interference of several experimentally indistinguishable processes separated in time due to a resonant capture of the electron

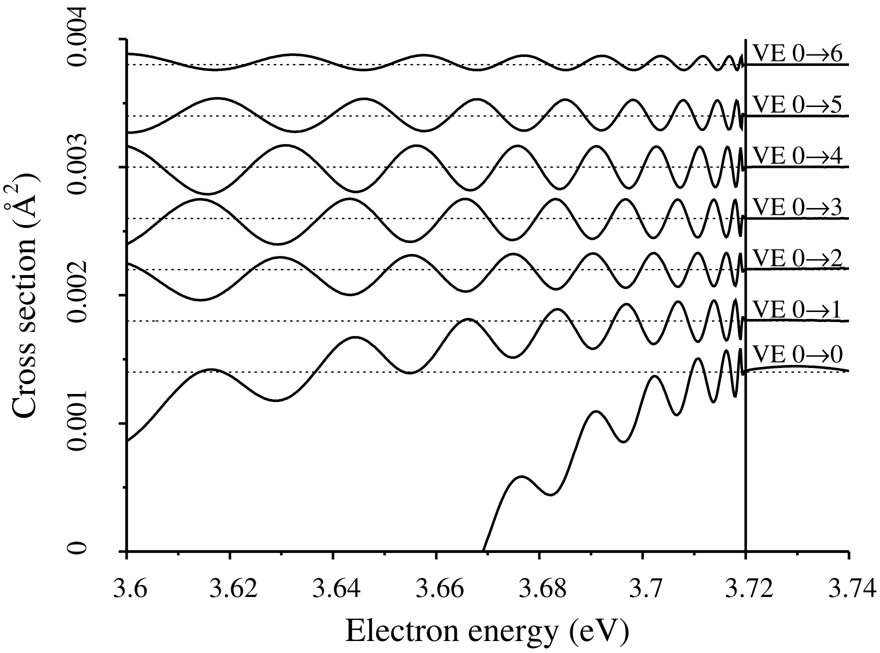

Figure 1.5: The cross sections of vibrational excitation of the molecule $H_2$ in the ground rovibrational state by the electron impact shown in the vicinity of the DA threshold (vertical line). A smooth background (given by linear approximation of the energy dependence of the cross section in the range $E = 3.72 - 3.74$ eV) was subtracted from each curve, and the results are vertically displaced for better visibility of the oscillations.

and the subsequent vibrational motion of the negative molecular ion which can also be of resonant character if there is a well in the anion potential outside the autodetachment region where long-lived states can appear as for $HCl^-$ (see outer-well resonances in Figure 1.4).

## 1.3 Towards polyatomic molecules

I participated in two studies where we considered multi-dimensional nuclear dynamics. In the first one we studied dissociative electron attachment and vibrational excitation processes in electron collisions with the CF3Cl molecule [12]. Only two degrees of freedom (the C-Cl symmetric stretch and the $CF_3$ umbrella mode) were included in our study and the cross sections were calculated within the LCP approximation with the complex potential energy surface obtained using the $R$-matrix fixed-nuclei scattering calculations. The results were only partially satisfactory and more elaborate study for this system should be undertaken in the future.

The study of the second polyatomic system was motivated by recent experiments performed by a group of Juraj Glosík at our faculty who have measured the reaction rate coefficients of the following processes

$$O^- + H_2 \xrightarrow{k_1} e^- + H_2O\,, \qquad O^- + H_2 \xrightarrow{k_2} OH^- + H\,, \tag{1.19}$$

$$O^- + D_2 \xrightarrow{k_3} e^- + D_2O\,, \qquad O^- + D_2 \xrightarrow{k_4} OD^- + D\,, \tag{1.20}$$

at very low temperatures up to 100 K.

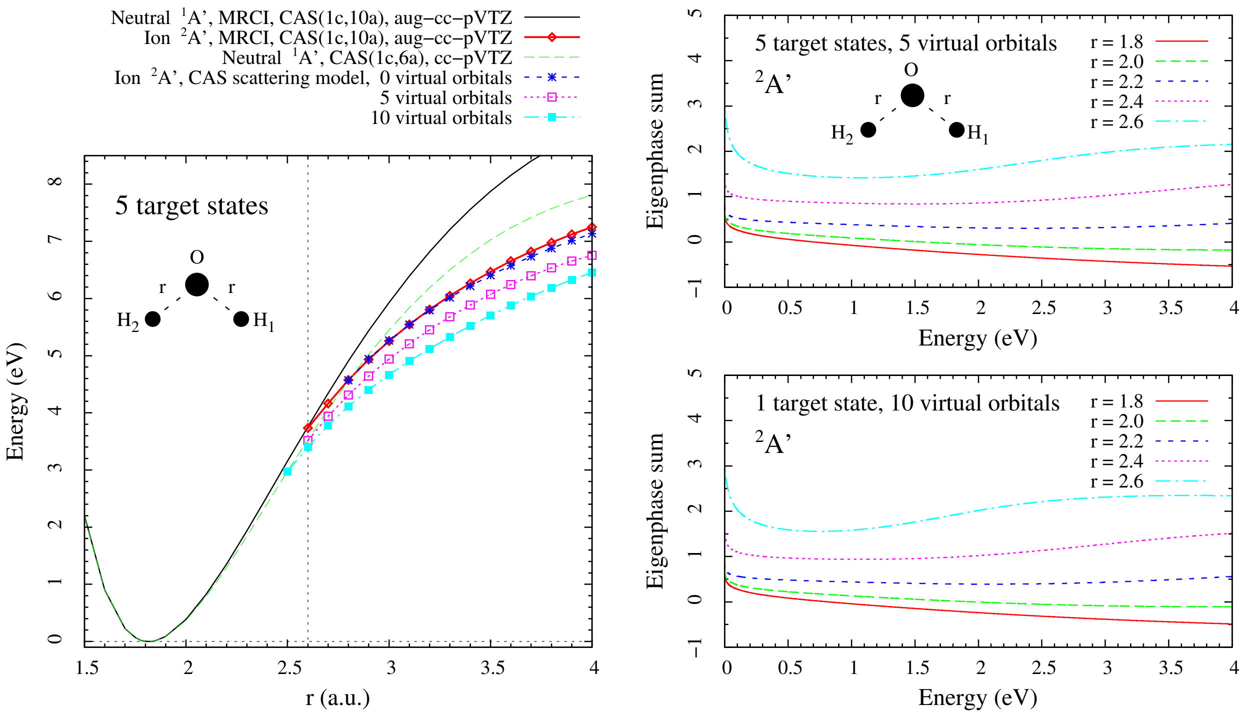

Figure 1.6: A cut of the potential energy surfaces of $H_2O$ and of $H_2O^-$ compared with results obtained using UKRmol codes for a few scattering models (left panel) and eigenphase sums (right panel) of fixed-nuclei electron scattering for several distances of O–H bond for the optimal scattering model.

Although the inverse process of dissociative attachment

$$e^- + H_2O \rightarrow O^- + H_2 \tag{1.21}$$

was studied in detail by Haxton *et al.* [77, 66] their calculations focused on higher energies (5–12 eV) where Feshbach resonances play an important role and were the LCP approximation can be used. On the other hand, for the processes (1.19) and (1.20) studied at very low energies only the lowest-lying states of $H_2O^-$ need to be taken into account but their potential energy surfaces have to be computed with sufficient accuracy (20–40 meV) to get reasonable results because the reaction $O^- + H_2 \rightarrow OH^- + H$ has threshold energy of only 0.3 eV. Only with relatively large quantum chemical calculations using Molpro [78] we got exothermic reaction with the threshold energy 0.23 eV. We calculated the full three-dimensional potential energy surface for the lowest-lying state $1\,^1A'$ of $H_2O$ molecule and for three lowest-lying states $1\,^2A', 2\,^2A'$ and $1\,^2A''$ of $H_2O^-$ at more than 30 000 geometries in all regions relevant for the processes (1.19) and (1.20) [13, 14]. We have found that all three states of $H_2O^-$ are connected through conical intersections of their potential energy surfaces, an example of which can be found in Figure 4 of [13]. These conical intersections are responsible for effective transfer among states because the system at very low energies is trapped in the vicinity of the conical intersections (again see Figure 4, right panel in [13]) and finally the system ends up at the lowest state $1\,^2A'$ with high probability of going into the autodetachment region and leading to the associative detachment process.

Unfortunately, the large quantum chemical model used to obtain the accurate potential

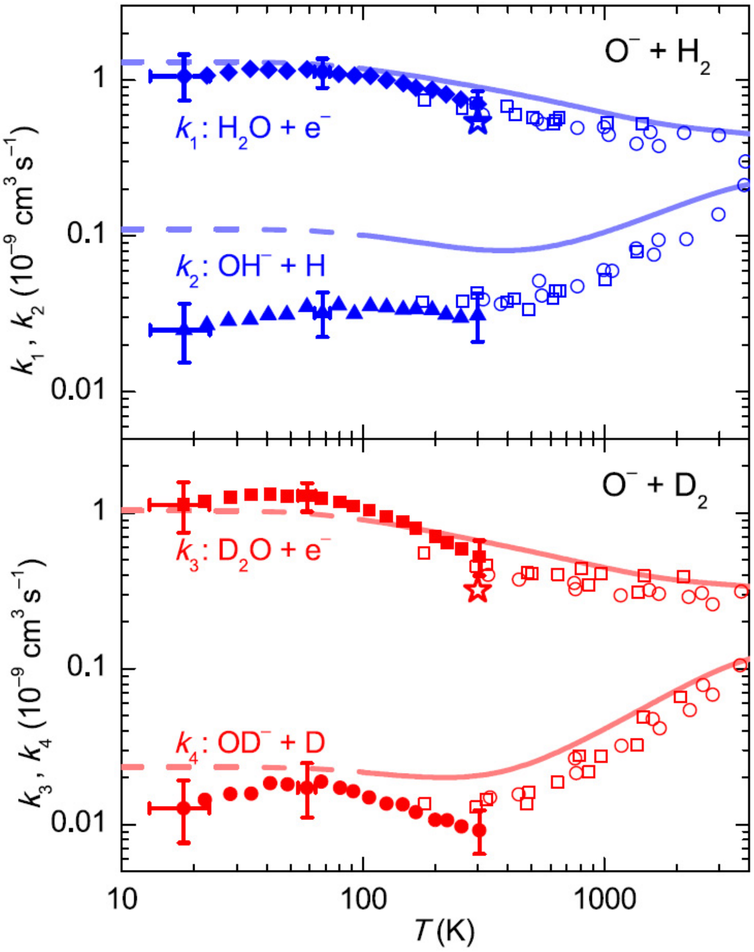

Figure 1.7: Temperature dependencies of the reaction rate coefficients for both channels of the reactions of $O^-$ with $H_2$ and $D_2$. The experimental data (full symbols) are compared with the results from the Monte Carlo simulations (lines). Open symbols indicate the experimental data of Viggiano *et al.* [79] (squares), McFarland *et al.* [80] (circles), and Jusko *et al.* [81] (stars). The part of the theoretical curve strongly dependent on the extrapolation of the calculated data is shown with dashed lines.

energy surface is impossible to use also in fixed-nuclei scattering calculations which are necessary to perform to obtain data for construction of a model for nuclear dynamics. The target molecule has to be described at a lower level of electronic correlation and one has to find a compromise between the accurate shape of the potential energy surface of $H_2O$ and feasibility of the scattering calculations. Therefore we compared several scattering models used in the UKRmol suite of codes [25] and found that reasonable model can be used for such calculations which will be consistent with the accurate potential energy surfaces in a sense that the relative position of the surfaces for the neutral molecule and negative molecular ion are approximately the same. Results were published in [14] and for a model with 5 target states included in the scattering calculations are also shown in Figure 1.6 for symmetric stretch. Currently we are running scattering calculations for many geometries in the autodetachment region to obtain enough information for construction of a nonlocal model for this system.

In our first work [13] we used a very simplified one-dimensional model to explain behaviour of the reaction rete coefficient for associative detachment at very low temperatures. The results were more or less in qualitative agreement with the experiment but it is clear that full description of three-dimensional nuclear dynamics will be necessary to explain the ratios and temperature dependence of the processes (1.19) and (1.20). Because we were not able to construct the full nonlocal model of the nuclear dynamics for this system yet we performed at least classical-trajectory Monte-Carlo simulations on the accurate potential energy surface of $H_2O^-$ with a simplified assumption that all trajectories which end in the autodetachment region lead to the associative detachment process. The results agreed surprisingly well with the experiment [15] as it is shown in Figure 1.7 but there are still some discrepancies (e.g. the rate coefficient for the reaction $O^- + H_2 \to OH^- + H$ is not reproduced well in this approximation) the origin of which we attribute to quantum effects, especially for lighter hydrogen compared to deuterium.

## 1.4 Conclusions and future work

My work on electron collisions with diatomic molecules was focused on the detailed evaluation of the various approaches to the nuclear dynamics of these processes. The two-dimensional model introduced in [1, 2] was successfully used to test validity of the local and nonlocal approaches to the nuclear dynamics and even extended to evaluate approximate approaches to the dissociative recombination process. The time-dependent calculations within this model also provided a deeper insight into the origin of oscillatory structures in the VE cross sections and their asymmetric peaks. Furthermore, my work on the real diatomic systems concentrated on interpretation of the cross sections, especially of vibrational excitation. We provided a clear explanation of such structures in the $e^- + H_2$ and other systems. We also began our first comprehensive study of a polyatomic system, the negative ion of the water molecule. Preliminary results based on classical-trajectory Monte-Carlo simulations on the accurate potential energy surfaces agree rather well with the experiment for collisions of $O^-$ with $H_2$ and $D_2$ but further studies based on the full quantum nonlocal approach to the nuclear dynamics are necessary. As a consequence of agreement of our results with experimental data we motivated the group of Juraj Glosík to perform measurements for collisions of $O^-$ with HD for we predicted an interesting isotopic effect for reactions resulting in the production of $OH^-$ or $OD^-$. These results were not published yet.

In the future we would like to continue in our investigation of electron collisions with diatomic molecules focusing mainly on molecules where the local complex potential approximation cannot be used at all such as LiH or BeH and on molecules which are important for applications but were not studied yet. But most of our attention will be focused on polyatomic systems for there is still a lot of challenging problems awaiting to be solved. Apart from our work on the water molecule, for which I believe we will be able to perform first complete quantum nonlocal nuclear dynamics in the near future, we have started work on other polyatomic molecules like HNCO motivated by recent experiments done in the group of Juraj Fedor at J. Heyrovský Institute of Physical Chemistry in Prague.

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# Chapter 2

# Original papers

## 2.1 Numerically solvable model for resonant collisions of electrons with diatomic molecules

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## 2.3 Time-dependent formulation of the two-dimensional model of resonant electron collisions with diatomic molecules and interpretation of the vibrational excitation cross sections

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## 2.4 Dissociative recombination by frame transformation to Siegert pseudostates: A comparison with a numerically solvable model

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## 2.5 Dissociative electron attachment and vibrational excitation of $H_2$ by low-energy electrons: Calculations based on an improved nonlocal resonance model

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## 2.9 Electron scattering in HCl: An improved nonlocal resonance model

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## 2.10 On irregular oscillatory structures in resonant vibrational excitation cross-sections in diatomic molecules

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## 2.11 Resonant inelastic collisions of electrons with diatomic molecules

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