

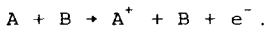
Introduction and overview

These notes correspond to a series of lectures given at the University of Aarhus (Denmark) under the general title, "Dynamics of negative ions", and mainly devoted to the theoretical study of bound state-continuum transitions in a low energy collision involving a negative ion. The physical situation consists in a low energy electron interacting with a neutral molecule. In the initial and final states of the collision, the electron energy can be positive or negative, i.e., the electron can be free or bound to a heavy particle to form a negative ion. Similarly, the energy of the heavy particle relative motion is either positive or negative corresponding to a bound molecule or to colliding heavy particles. A few different collision processes pertain to this physical situation:

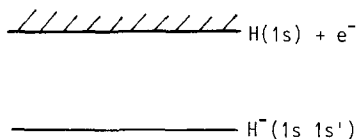
- Collisional detachment: $A^- + B \rightarrow A + B + e^-$. Due to the relative motion of the A and B heavy particles, one of the electrons initially bound in the A^- ion is ejected into the continuum.
- Associative detachment: $A^- + B \rightarrow AB + e^-$. This process is analogous to the previous one. It can be very important at thermal collision energies, in systems where the electron affinity of A is smaller than the dissociation energy of the neutral AB molecule.
- Dissociative attachment: $e^- + AB \rightarrow A^- + B$. It is simply the reverse process of associative detachment, and they are indeed linked by time reversal. This process can be seen as an energy transfer from the electronic motion to the relative motion of the heavy particles. It is thus linked to:

- Vibrational excitation: $e^- + AB(v) \rightarrow AB(v') + e^-$. The two last processes only differ by the amount of energy transferred from the electron to the vibrational motion and should thus be treated in the same theoretical frameworks.

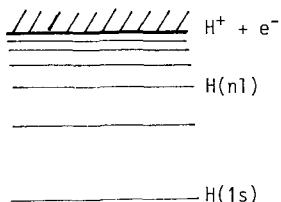
The above processes, concerning negative molecular ions, are analogous to systems with other charge states. For example, collisional detachment could be thought to be similar to collisional ionization in a neutral system:



However, negative ions have rather special characteristics, as compared with neutral atoms. In general, binding energies of the negative ions are rather small, so the energy change involved in collisional detachment is smaller than that involved in an ionization process. The negative ion spectrum is also rather different from that of a neutral. For example, the electronic structure of the H^- ion can be described by the $1s1s'$ configuration (open shell with two non orthogonal orbitals). The $1s$ inner orbital is very close to the $1s$ atomic orbital of the hydrogen atom and the $1s'$ orbital is very diffuse and loosely bound. This outer electron will be the most affected by a collision process, and the only thing that can happen to it is detachment, since there is not any excited state of the $1snl$ type. The H^- ion bound state spectrum only contains one level:



In contrast, a neutral system contains an infinite series of singly excited states converging to the positive ion. For example, the spectrum of the H atom is:



In such systems, detachment is a way to study bound-free transitions as a one-electron process, without any associated excitation process, while ionization appears to be the limit of a series of excitation processes. Indeed, negative ions, such as H^- , have excited states although unstable. For H^- , these correspond to the attachment of electrons on excited hydrogen atoms (like e.g. $2s^2$); their energy is much higher and they can only be formed by two electron processes involving the inner electron. The small binding energy of a negative ion has another consequence: the loosely bound electron occupies a very diffuse orbital which should yield a large geometrical factor to the detachment cross section. A priori, one could then expect large

detachment cross sections associated to one-electron processes.

In the lectures, the study of bound state continuum transitions in molecular negative ions is limited to the domain of low collision energies. For the heavy particles, this is the domain of the so-called molecular picture of atomic collisions. Indeed, in this domain, the heavy particle velocity is much smaller than the electron velocities, due to the large mass ratio and heavy particles and electrons live on different time scales. This allows for the quasi separation of the electronic and nuclear movements and leads to the Born-Oppenheimer approximation in molecular physics. For an H^- ion, the molecular domain corresponds to a collision energy smaller than 1.5 keV. The evolution of the quasi molecular ion formed by a negative atomic ion colliding on a target can be treated in a way similar to that of a vibrating molecule like, e.g., in the course of an electron-molecule collision. All the collision processes listed above, although they correspond to rather different experimental situations, can be described as a low-energy electron interacting with a quasi molecule and could then be theoretically analysed in the same framework.

The type of problems defined above can be approached in different ways. The present lectures do not aim at an exhaustive presentation of all the possibilities, they mainly concentrate on one type of treatment, the effective range approximation. The problem of bound state-continuum transitions is a rather difficult one to handle, because of the a priori infinite number of states to consider, and therefore, various approximations were looked for. Those can be performed on the way the bound state continuum interaction is treated, by dropping certain aspects of it, like, e.g., in the local resonance approxima-

tion. The effective range approximation (ERT) approaches the problem in a different way: it performs the approximation on the molecular negative ion system to be studied, by taking advantage of the low energy of the outer electron; the collision problem is then sufficiently simplified to allow for an exact treatment of the dynamics. One of the main characteristics of the ERT formalism is that it treats in a unified manner bound and free motions, both for the electron and for the vibrational motion of the molecule. In this way, the problems arising from the presence of a continuum are much simplified. This type of theoretical approach, consisting in a modelling of the collision system in order to be able to fully handle the collision dynamics has a double interest. First, it provides a very efficient way of understanding and analysing the collision dynamics: an exact treatment within a given framework enables to test various approximations, interpretations, as well as the effect of the various factors on the collision process. Secondly, the modelling of the collisional system can be rather easily linked with static ab initio calculations. The ERT formalism requires a small number of parameters to describe a molecular negative ion system; as a consequence, these few parameters can be obtained from limited ab initio calculations on the static system. The ERT thus provides a parametrization of static ab initio calculations that leads to a tractable way to handle the collision dynamics. Indeed, the number of ERT parameters being small, they can also be determined in an empirical manner.

The contents of the various chapters is as follows:

Chapter 1 briefly outlines the formalism associated to the molecular picture of atomic collisions, in the case of a classical description of the heavy particle motion. The set of coupled equations describing bound state continuum transitions being recognized difficult to handle, the local complex potential approximation (LCP) is presented, together with some indications on its derivation and on the conditions for its validity. A few effects predicted by the LCP and connected to the local character of the bound state-continuum transitions are shown on various experimental results. All these examples pertain to ionization processes via two electron interactions. In contrast, for the attachment-detachment process via one-electron interactions, the LCP was very early recognized to fail, thus requiring further investigation.

Chapter 2 presents a brief summary of the quantal treatment of potential scattering. Special emphasis is put on the threshold laws, i.e., on the behaviour of the various scattering properties when the collision energy goes to zero, as well as on the fate of a bound state when the potential, which binds it, weakens. The effective range approximation, based on the limit of the scattering when the energy goes to zero, is then presented together with a few of its applications to static problems.

Chapter 3 is devoted to the collisional detachment process. The simplest version of the ERT, the zero range potential (ZRP) approximation is shown to allow for a direct numerical solution of the time dependent Schrödinger equation describing the detachment process. This numerical procedure yields the electron wavefunction as a function of time along the trajectory and therefore a picture of how is detachment occurring. The H^- -He and Ne collisional systems are presented as illu-

strative examples.

In chapter 4, the ZRP method is applied to the problem of associative detachment, with the Cl^- , F^- -H thermal collisions as examples. The low collision energy, as well as the bound vibrational motion in the final state makes a quantal treatment of the nuclear motion necessary.

Chapter 5 is an introduction to the dynamics of the vibrational motion in the course of an electron-molecule collision. The two main limits are examined: when the collision time is short compared to the vibrational period, a sudden approximation should be valid, whereas if the electron can be trapped by the target molecule, the collision time is considerably increased and a resonant formalism should apply. Indeed, the ERT formalism making no assumption on the collision time can apply in both situations and examples of its use are presented in the last two chapters.

Chapter 6 discusses the vibrational excitation and dissociative attachment processes when the active electron has a spherical symmetry (s wave) and thus when no resonant state can be invoked as an intermediate in the process. Examples are shown on the e^- -HCl, HF and SF_6 systems. Chapter 7 is devoted to the e^- - H_2 collisional system at low energy, where the active electron has a p wave symmetry, thus allowing for the existence of an H_2^- resonant state, which will be seen to be highly unstable. Results obtained both in the non resonant ERT formalism and in the non local resonant formalism of Domcke et al. are presented in order to discuss in detail the characteristics of the collision process. Finally some summarizing conclusions are presented.

A small bibliography is given at the end of each chapter. It is not intended to be exhaustive, it only selects a few representative references, either because they are discussed in the text, or because they present features, aspects or approaches which are absent from the text. This bibliography is mainly intended to provide a basis for further reading. It also contains references to review papers where more comprehensive bibliographies can be found.

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