

World Scientific Lecture Notes in Physics, Vol. 15

DYNAMICS OF NEGATIVE IONS

by

Jean Pierre Gauyacq

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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:

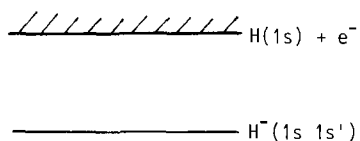
- Collisional detachment: $A^- + B \rightarrow A + B + e^-$. Due to the relative motion of the A and B heavy particles, one of the electrons initially bound in the A^- ion is ejected into the continuum.
- Associative detachment: $A^- + B \rightarrow AB + e^-$. This process is analogous to the previous 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.

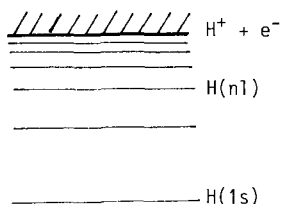
The above processes, concerning negative molecular ions, are analogous to systems with other charge states. For example, collisional detachment could be thought to be similar to collisional ionization in a neutral system:



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 detachment is 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.

Acknowledgements: The lectures corresponding to these notes were given at the Institute of Physics of the University of Aarhus in the end of 1985. I gratefully acknowledges the Institute for its financial support during my stay and especially B.Fastrup and his colleagues for their kind and friendly hospitality. Thanks are also due to Mrs. I.Schmidt for typing the manuscript.

CHAPTER 1

Atom(ion)-atom collisions in the molecular regime

At first glance, an atom-atom collision may look rather complicated, because of the large number of particles interacting together. Consequently, the number of variables needed to describe the process is too large for an exact solution to be attempted. However, the collisional system is formed of rather different kinds of particles: nuclei and electrons, and this yields the basic idea of the so-called molecular description of atomic collisions (as well as of the Born Oppenheimer approximation widely used in molecular physics).

Because of the large mass difference between nuclei and electrons, if the collision energy is not too large, one has the following relation between velocities:

$$v_{\text{Nuclei}} \ll v_{\text{electron}} \quad (1)$$

i.e., the electrons are living in a much shorter time scale than do the nuclei. Thus one gets the idea of treating each movement of a given scale "separately" from the other movements pertaining to different time scales.

The electron movement is studied with the nuclei held fixed. This corresponds to the electronic Hamiltonian H_{el} , which contains the electron kinetic energy, and all the interactions between electrons, between electrons and nuclei, and between nuclei. One can then define electronic states ϕ_{el} which are solutions of the electronic problem

with fixed nuclei:

$$H_{el} \phi_{el}^i = E_i(R) \phi_{el}^i \quad (2)$$

$\xrightarrow{\text{index}} \phi_{el}^i(\vec{r}, R)$

$\swarrow \quad \searrow$
 variables parameter
 (electron coordinates) (internuclear distance)

The idea of treating separately the electronic and nuclear movement results in a wave function for the total system (moving electrons and nuclei) which is a product of an electronic and a nuclear term:

$$\phi_{el}^i(\vec{r}, R) F^i(\vec{R}) \quad (3)$$

This wave function corresponds to the Born-Oppenheimer approximation. One can go back to the initial condition for this approximation. A critical velocity for the nuclei can be obtained as the orbital velocity of the atomic electron (indeed these velocities will be modified at small distances).

For H^- , the binding energy is .75 eV and this leads to a critical collision energy around 1400 eV.

For Cl^- , the binding energy is around 3.5 eV and the critical energy is now around 200 keV.

The wave function (3) contains only one electronic state and thus can only describe the elastic scattering of two atoms, and excitation processes are out of its reach! One now considers an expansion over the electronic states of the total wave function Ψ_T :

$$\Psi_T = \sum_i \phi_{el}^i(\vec{r}, R) F^i(\vec{R}) \quad (4)$$

The sign $\sum_i$ is a complete sum, it incorporates both the bound states

and the continuum states defined in (2). The equation (4) appears to be nothing but an expansion over a complete basis set, and then does not introduce any approximation! The approximation will lie in the truncation of the infinite sum in (4); the idea is that the B.O. separation of nuclear and electronic movement is almost true, and that the departures from it can be treated by only introducing a few terms in (4).

Coupled equations in the semiclassical region

If the energy of the heavy particles is large enough, their movement can be treated classically, i.e., there exists a trajectory, a relation between R and the time t .

The total wave function becomes a function of time:

$$\Psi(t) = \sum_i C_i(t) \phi_{el}^i(\vec{r}, t) \quad (5)$$

which has to be the solution of the time dependent Schrödinger equation:

$$i \frac{\delta \Psi}{\delta t} = H_{el} \Psi \quad (6)$$

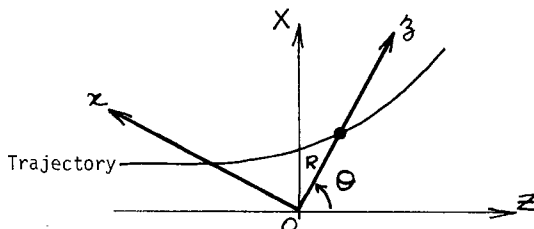
with the following boundary condition: $|C_i(-\infty)|^2$ vanishing except for the initial state of the collision, where it amounts to one. One has then the following picture; the system is travelling along the potential energy curves $E_i(R)$ of the various ϕ_{el}^i states with a probability amplitude $C_i(t)$. Due to the collision, these amplitudes vary with time, and the system jumps from one state to the other.

After bringing the expansion (5) into (6) and projecting over the various electronic states, one gets:

$$i \frac{dC_i}{dt} = E_i(t)C_i + i \sum_j C_j(t) \langle \phi_i^{el} | H^{el} | \phi_j^{el} \rangle - i \sum_j C_j(t) \langle \phi_i^{el} | \frac{\delta}{\delta t} | \phi_j^{el} \rangle \quad (7)$$

(Note: if the ϕ_i^{el} are defined as the solution of the electronic problem with fixed nuclei, then they are not coupled by H_{el} ; however, we will demonstrate the coupled equations for an arbitrary set of ϕ_i^{el} functions).

The derivative $\delta/\delta t$ only operates on the ϕ_i^{el} functions via their dependence on the internuclear distances, i.e. the trajectory.



Two sets of coordinates: Oxyz and OXYZ (The trajectory is contained in a plane)

$$\frac{\delta}{\delta t} = \frac{\delta}{\delta R} \times \frac{dR}{dt} + \frac{\delta}{\delta \theta} \times \frac{d\theta}{dt} \quad (8)$$

One must be careful with the above derivatives. Indeed, the Schrödinger equation is written in a galilean frame (the laboratory frame OXYZ) as well as all the derivatives in (8). However, the functions ϕ_i^{el} are defined in the molecular frame (e.g. quantized along the internuclear axis) Oxyz.

The difference between the two frames is only angular:

$$\theta_{el,Oxyz} = \theta_{el,OXYZ} - \theta$$

electronic angular variables around Oy,OY

Thus,

$$\frac{\delta}{\delta\theta} \Big|_{OXYZ} = \frac{\delta}{\delta\theta} \Big|_{Oxyz} + \text{electrons} \frac{\delta}{\delta\theta_e} \Big|_{Oxyz} \times \frac{\delta\theta_{e,Oxyz}}{\delta\theta}$$

$$\frac{\delta}{\delta\theta} \Big|_{OXYZ} = \frac{\delta}{\delta\theta} \Big|_{Oxyz} - iL_y$$

With L_y : projection of the electronic angular momentum on Oy.

The coupled equations are then:

$$i \frac{dC_i}{dt} = E_i C_i(t) + \sum_j C_j(t) \langle \phi_i^{el} | H_{el} | \phi_j^{el} \rangle$$

$$+ \sum_j \left(-i \frac{dR}{dt} \right) \langle \phi_i^{el} | \frac{\delta}{\delta R} | \phi_j^{el} \rangle C_j(t)$$

$$+ \sum_j \left(-\frac{d\theta}{dt} \right) \langle \phi_i^{el} | L_y | \phi_j^{el} \rangle C_j(t) \quad (9)$$

Only a few details on these equations, which are not the purpose of the lectures. The r.h.s. of (9) contains an elastic term, which yields the quantal phase factor $\exp(-i\int E dt)$. It contains a coupling term, with the selection rule $\Delta\Lambda=\pm 1$ (Λ projection of the electronic angular momentum on the internuclear axis), and the operator L_y ; it is called "rotational coupling" and is a dynamical coupling, because of the $d\theta/dt$ factor.

Two terms are coupling the same states (selection rule $\Delta\Lambda=0$): they correspond to the operators H_{el} and $\delta/\delta R$. Since one can always perform a basis set change on the ϕ_i^{el} , it is possible to favour one term or the other:

- * if $\langle \phi_i | H_{el} | \phi_j \rangle = 0$, the ϕ_i basis is said adiabatic, the coupling term is via $\delta/\delta R$ which is dynamical, because of the velocity factor.
- * if $\langle \phi_i | \frac{\delta}{\delta R} | \phi_j \rangle \ll \langle \phi_i | H_{el} | \phi_j \rangle_{el}$ the basis set is said diabatic, the couplings are static via the H_{el} operator.

Of these two possibilities, one chooses usually the basis set with the smallest couplings. At low velocities $v \rightarrow 0$, the adiabatic basis should be preferred, and diabatic states should be looked for at higher velocity.

Intuitive picture: if one can split H_{el} into two parts, H_0 and H_1 with $\langle H_0 \rangle \gg \langle H_1 \rangle$, then the time scales τ_0 and τ_1 associated with H_0 and H_1 will be quite different: $\tau_0 \ll \tau_1$; and then the B.O. separation may be true for the H_0 part and not the H_1 part, i.e., the nuclear characteristic time τ_N may be like: $\tau_0 \ll \tau_N \ll \tau_1$. In such a case, diabatic states which only diagonalize H_0 (and not the complete H_{el}) should be useful, and should lead to almost decoupled equations.

If we consider now the coupled equations for a bound free problem, the sum sign Σ must include the continuum infinity; the method leads to an infinite set of coupled equations with a continuous index. The approximation of truncating the expansion (5) to only a small number of electronic states cannot be used if one expects continuum states to be populated. This was a very good incentive to look for further approximations to treat the bound free transition problem.

One of the methods the most widely used to avoid the infinite set of coupled equations is the local complex potential approximation (LCP). It originates from the Fermi golden rule, i.e. from the perturbation treatment of the decay of a quasi stationary state ϕ_d , embedded in a continuum ϕ_e and coupled to it. The main result (see any quantum

mechanics text book) is that the state acquires a width Γ , equal to the decay rate of the quasi stationary state:

$$\Gamma = 2 |\langle \phi_d | H_{el} | \phi_e \rangle|^2 \rho(E)$$

density of continuum states.

The state is also shifted by a quantity:

$$\Delta = \mathcal{P} \int d\epsilon' \frac{|\langle \phi_d | H_{el} | \phi_{\epsilon'} \rangle|^2}{\epsilon - \epsilon'}$$

principal part of the integral.

This can be derived for a time independent Hamiltonian. The basic idea of the LCP approximation is an adiabatic idea: at low velocities the system should follow the static problem i.e. should decay with the width given by the Fermi golden rule. The quasi stationary state is then represented by a complex potential

$$V(R) = \langle \phi_d | H_{el} | \phi_d \rangle - i \frac{\Gamma(R)}{2} + \Delta(R).$$

Then the solution of the collision problem is very simple, one has only to consider the quantal phase

$$\exp(-i \int V(R) dt),$$

which contains a survival factor $\exp(-\int (\Gamma/2) dt)$.

How to demonstrate the LCP?

We will consider the problem of a state ϕ_d , only coupled with a continuum ϕ_e by the electronic Hamiltonian. The continuum states are assumed to be uncoupled. The coupled equations (9) are:

$$\begin{aligned} i \frac{dc}{dt} &= E_d c(t) + \int d\epsilon \langle \phi_d | H_{el} | \phi_e \rangle C_e(t) \\ i \frac{dC_e}{dt} &= E_e C_e(t) + \langle \phi_e | H_{el} | \phi_d \rangle c(t). \end{aligned} \quad (10)$$

With the following change of function:

$$\begin{aligned} b(t) &= \exp(-i \int_{t_0}^t E_d dt') c(t) \\ b_e(t) &= \exp(-i \int_{t_0}^t E_e dt') C_e(t). \end{aligned}$$

The second equation becomes

$$i \frac{db_e}{dt} = \langle \phi_e | H_{el} | \phi_d \rangle e^{-i \int_{t_0}^t (E_d - E_e) dt'} b(t).$$

When brought into the first equation, it yields:

$$\begin{aligned} i \frac{db}{dt} &= -i \int d\epsilon V_{d\epsilon}(t) e^{+i \int_{t_0}^t (E_d(t'') - E_e) dt''} \\ &\quad \times \int_{t_0}^t dt' V_{ed}(t') e^{-i \int_{t_0}^t (E_d - E_e) dt'} b(t') \end{aligned} \quad (11)$$

with the notation $\langle \phi_e | H_{el} | \phi_d \rangle = V_{ed}(t)$ (it depends on time via the trajectory). Equation (11) is equivalent to (10). It is a non local expression, since the evolution at time t (db/dt) depends via an integral upon the situation of the system at all the previous times t' . A local expression computes the evolution at time t (db/dt) with

the only knowledge of the system at time t ($b(t)$ and various couplings).

Let us examine how equation (11) can be transformed into a local expression. The double integral in (11) is:

$$\int_{t_0}^t dt' \int d\epsilon V_{d\epsilon}(t) V_{\epsilon d}(t') \exp(-i \int_t^{t'} (E_d(t'') - E_\epsilon) dt'') \times b(t').$$

The dt' integral contains a phase factor rapidly varying with t' , and we could evaluate it by the stationary phase approximation. The stationary point is given by

$$\frac{\delta}{\delta t'} \left[\int_t^{t'} (E_d(t'') - E_\epsilon) dt'' \right] = 0$$

$$E_d(t') = E_\epsilon \quad (12)$$

i.e. the state ϕ_d mainly decays to the continuum state which has the same energy. In the double integral, the main contributions come from the region of stationary phase, i.e. from the line defined by (12). We can thus set in the integral, all the ϵ equal to $E_d(t')$

$$\frac{db}{dt} = - \int_{t_0}^t dt' \int d\epsilon V_{dE_d(t')}(t) \times V_{E_d(t')\epsilon}(t') e^{-i \int_t^{t'} (E_d(t'') - E_\epsilon) dt''} b(t')$$

E_ϵ is equal to ϵ plus the potential energy of the bottom of the continuum E_N . The integral over ϵ is thus $\int d\epsilon e^{i\epsilon(t-t')}$; it yields a $\delta(t'-t)$ if the continuum is broad enough, so that equation (11) becomes:

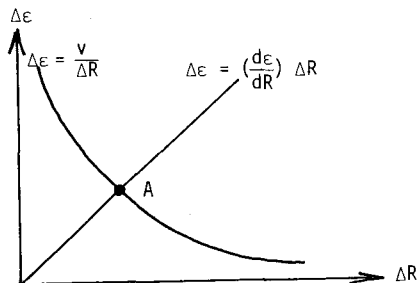
$$\frac{db}{dt} = -\pi |V_{dE_d}(t)|^2 b(t) \quad (13)$$

Thus the localization appears through the relation $E_\epsilon = E_d(t)$. So even

with a classical motion of the nuclei, the non local character comes from a quantal effect: at each time, the decay of ϕ_d populates all the continuum states, and all the corresponding amplitudes interfere. However, if the phases are large enough, most of these interferences are destructive and in fact the system behaves almost locally. The condition for the derivation is then that nothing happens over the size of the minimum wave packet in the continuum, or in other words that in (11) the stationary phase approximation is valid. This leads to the following conditions:

- ϕ_d, ϕ_e and their couplings can be defined;
- $V_{de}(t)$ slowly varying with t and ϵ ;
- $b(t)$ slowly varying with t , i.e., Γ small.

The size of the wave packet can be obtained from the stationary phase region. Let us derive it directly. We are looking for a localization $\epsilon = E_d(t) - E_N(t) = E_d(R) - E_N(R)$ with an uncertainty $\Delta\epsilon$. It corresponds to a time uncertainty: $\Delta t = \Delta R/v = \Delta\epsilon / (d\epsilon/dR)v$ given by the time during which the decay populates the $\Delta\epsilon$ states. This in turn yields an energy uncertainty $\Delta\epsilon \sim 1/(\Delta t)$. In the $\Delta\epsilon, \Delta R$ plane, the best uncertainty is the point A:



The size of the wave packet in the continuum is given by:

$$\begin{aligned}\Delta\epsilon &= \sqrt{v \, d\epsilon/dR} \\ \Delta R &= \sqrt{v/(d\epsilon/dR)} \\ \Delta t &= \frac{1}{\sqrt{v \, d\epsilon/dR}}\end{aligned}\tag{14}$$

It is thus possible to re-express the above conditions for the locality derivation:

- ϕ_d, ϕ_ϵ can be defined
- $V_{d\epsilon}(t)$ must be independent of ϵ and t over the $\Delta\epsilon, \Delta t$ scale
- $\Gamma < \Delta\epsilon = \sqrt{v(d\epsilon/dR)}$.

A few remarks can be made about the last condition. First it states that Γ must be small, this is not surprising since if the $\phi_d \phi_\epsilon$ coupling becomes too strong, ϕ_d will lose all its quasistationary character and one cannot expect the LCP to be valid. As a second remark, if $v \rightarrow 0$, the condition cannot be fulfilled; indeed, if $v \rightarrow 0$, quantal effects associated with the spreading of ϕ_d over continuum states will become more important.

The above derivation of the LCP approximation is not the most precise, however, it remains rather simple and gives some insight into the origin of the non local aspects. Other approaches of this problem can be found in the following articles.

- Configuration interaction (CI) approach of the static problem:
Fano 1961, Phys.Rev.124, 1866
- Non local aspects: Nakamura 1969, J.Phys.Soc.Japan 26, 1473

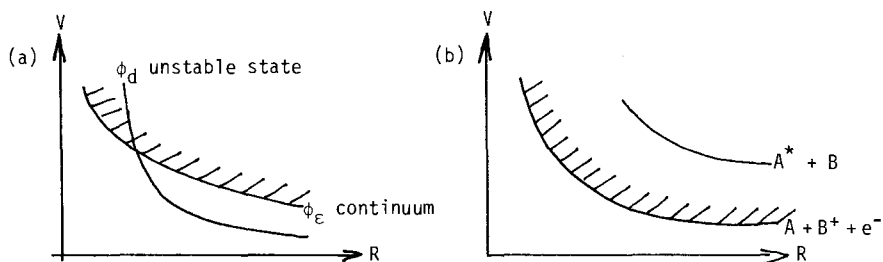
Bieniek R. 1978, Phys.Rev.A 18, 392

- Attempts to treat the non local decay rate: Wang and Delos 1984, Phys.Rev.A 29 542
- Another derivation of the LCP: Demkov Y. and Osherov V., Sov. Phys.JETP 1968, 26 916

Local complex potential approximation

see e.g. the paper by W.H.Miller, J.Chem.Phys.1970, 52, 3563

As explained above, the effect of the continuum interaction on the quasi bound state evolution reduces to a width $\Gamma(R)$, only function of the internuclear distance R , which yields the decay rate. It can be applied to the following situations



It has been very successful in describing Penning ionization process

(b). This process is a rather favourable case: indeed ϕ_ϵ and ϕ_d are rather easy to define as $B^+ + e^-$ and A^* . The ϕ_d state decays by a two-electron interaction similar to an Auger process: the excited electron of A^* fills an empty low orbital of A , while a B electron is ejected into the continuum.

*Classical description of the nuclear motion

Let $\Gamma(R)$ be the decay rate of the state.

If $N(R)$ is the population of the ϕ_d state at internuclear distance R , then the decay equation is:

$$dN = -N\Gamma dt \quad (15)$$

With a classical trajectory for the nuclei

$$dt = \frac{dR}{v_R} = \frac{dR}{v_\infty \sqrt{1 - V/E - b^2/R^2}}$$

with v_R = radial velocity

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v_{∞} = asymptotic velocity

$V(R)$ = real part of the LCP

b = impact parameter.

The evolution equation is very easily integrated and yields for the way in of the trajectory

$$N_{in}(R) = \exp\left(-\int_R^{\infty} \frac{\Gamma dR}{v_R}\right)$$

and way out:

$$N_{out}(R) = \exp\left(-\int_{R_0}^{\infty} \frac{\Gamma dR}{v_R}\right) \times \exp\left(-\int_{R_0}^R \frac{\Gamma dR}{v_R}\right) \quad (16)$$

with R_0 turning point of the trajectory. The ionization probability at the end of the collision is then:

$$P_{ioniz} = 1 - P_{survival} = 1 - \exp\left(-2\int_{R_0}^{\infty} \frac{\Gamma dR}{v}\right) \quad (17)$$

And the total cross section $\sigma_{ioniz} = \int 2\pi b P_{ioniz}(b) db$. And the classical differential cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{in} = \left(\frac{d\sigma}{d\Omega}\right)_{class} P_{ioniz}(b(\theta))$$

where $(d\sigma/d\Omega)_{class}$ is the classical scattering cross section along a potential; it also yields the relation between θ and b .

At this point, one can note that the continuum aspect has been completely eliminated. The only input of the calculation is the local complex potential $(V - i\Gamma/2)$. In particular, the actual shape of the continuum potential energy curve, as well as of the interactions do

not appear.

*Spectrum of ejected electrons

The probability for the system to ionize between the distances R and $R+dR$ is:

$$dP_{\text{ion}} = dP_{\text{ion}}^{\text{in}} + dP_{\text{ion}}^{\text{out}} = \frac{\Gamma(R)}{v_R} dR e^{-\int_R^{\infty} \Gamma \frac{dR}{v_R}} e^{-\int_{R_0}^R 2\Gamma \frac{dR}{v_R}}$$

which can be transformed into an energy spectrum for the ejected electrons: $Sp(\epsilon)$:

$$Sp(\epsilon) = \frac{dP_{\text{ion}}}{dR} \frac{dR}{d\epsilon} = \frac{dR}{d\epsilon} \frac{\Gamma}{v_R} e^{-\int_R^{\infty} \Gamma \frac{dR}{v_R}} e^{-2\int_{R_0}^R \Gamma \frac{dR}{v_R}} \quad (18)$$

with $\epsilon(R)$ the energy difference between the quasi bound state and the bottom of the continuum at distance R .

A few remarks can be made about formula (18):

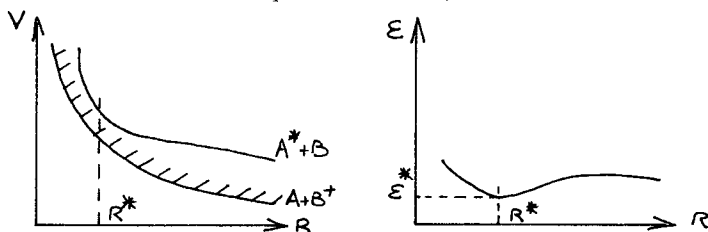
- At the classical turning point of the trajectory R_0 , the radial velocity vanishes, and that causes a divergence of the spectrum $Sp(\epsilon)$. However, if one considers the integral of $Sp(\epsilon)$ like in (17):

$$\int_{R_0}^{\infty} \Gamma \frac{dR}{v_R} = \int_{R_0}^{\infty} \frac{\Gamma(R) dR}{\sqrt{1 - V/E - b^2/R^2}}.$$

The divergence of the integrand behaves like $1/(\sqrt{R-R_0})$ and the integral converges. Thus for each trajectory, the spectrum of ejected electrons has a divergence which is integrable (indeed a

quantal calculation will suppress this divergence). The position of the divergence depends on b and E and will thus appear only in differential studies

- If the function $\epsilon(R)$ presents an extremum ϵ^* , then the function $R(\epsilon)$ is multivalued and (18) has to be modified accordingly. The spectrum $Sp(\epsilon)$ diverges at the $\epsilon=\epsilon^*$ energy (again a quantal calculation will show only an extremum).



- The divergence only appears in $Sp(\epsilon)$ and not in dP_{ion}/dR . It only depends on $\epsilon(R)$ and is thus a characteristic of the collisional system, a signature of it.

*Semiclassical picture:

It is possible to develop a semiclassical formalism for the LCP approximation (see the Miller paper). For this purpose one defines amplitudes instead of probabilities: For the process Q , one has the amplitude f_Q :

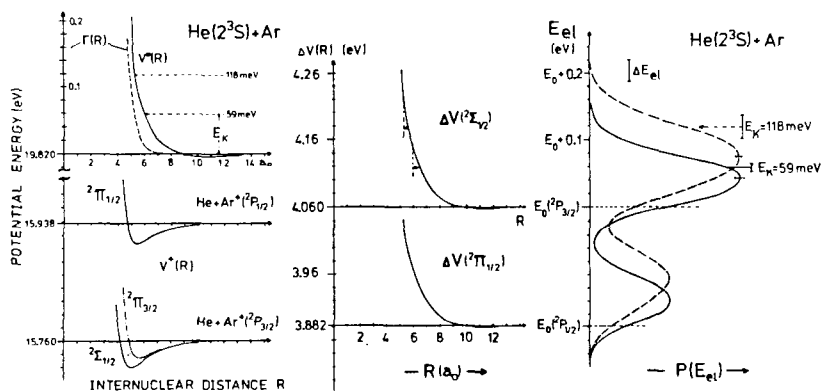
$$f_Q = [P_Q]^{1/2} e^{i\varphi_Q}$$

↑ Classical probability
 ↖ JWKB phaseshift

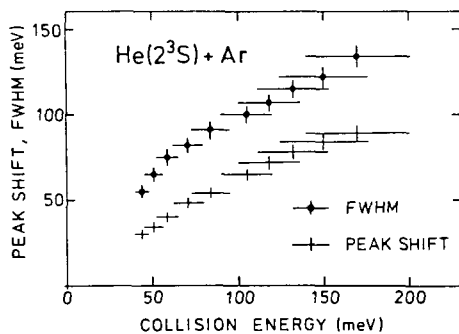
These phases will lead to interferences between ionization on the way in and out of the collision; these interferences depend on ϵ and on the trajectory and will thus appear only in differential measurements

of both ϵ and the scattering angle. If the $\epsilon(R)$ function has a minimum, the semiclassical treatment will also generate oscillations in the differential cross sections and spectra, similarly to a rainbow structure.

We will now examine a few experimental results which exhibit the various features detailed above. First we will consider results for the Penning ionization in He metastable H and Ar collisions. (The examples are taken from an invited talk by H.Hotop at the XI ICPEAC in Kyoto 1979; book page 271). They are measurements of the energy spectrum of ejected electrons; they are not associated with a differential analysis of the heavy-particle scattering and are thus sums over all the possible trajectories.



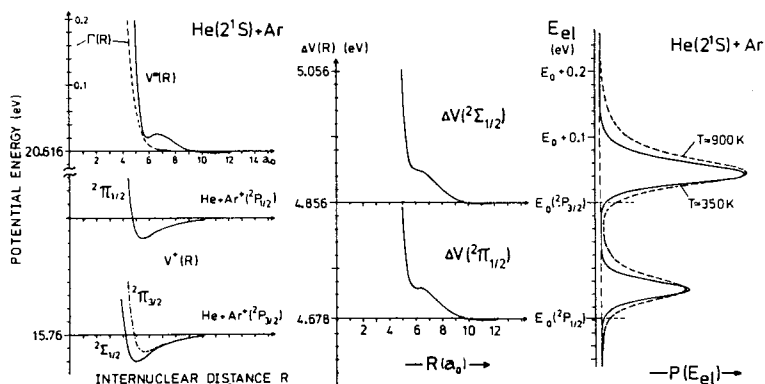
Potential energy curves, difference potentials, and electron spectra at the two collision energies of 59 meV and 118 meV for $\text{He}(2^3\text{S}) + \text{Ar}$



Dependence of the peak energy shift Δp and of the peak width w on collision energy for the $\text{He}(2^3\text{S}) + \text{Ar}$ system.

He(2^1S) + Ar system

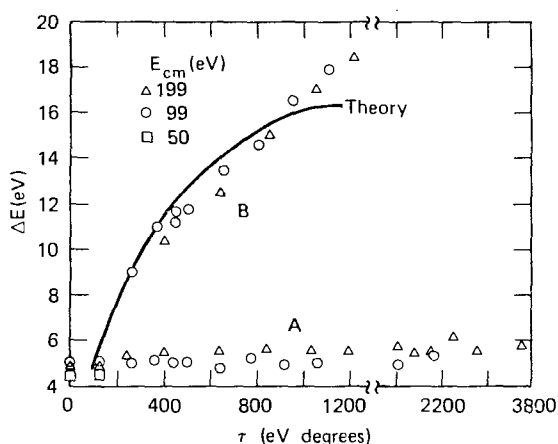
Two exit channels ($\text{Ar} + {}^2P_{3/2}$, ${}^2P_{1/2}$) are present, and in both of them the $\epsilon(R)$ function exhibits a shoulder. It results in a peak in the electron energy spectrum which does not move when the collision energy changes.



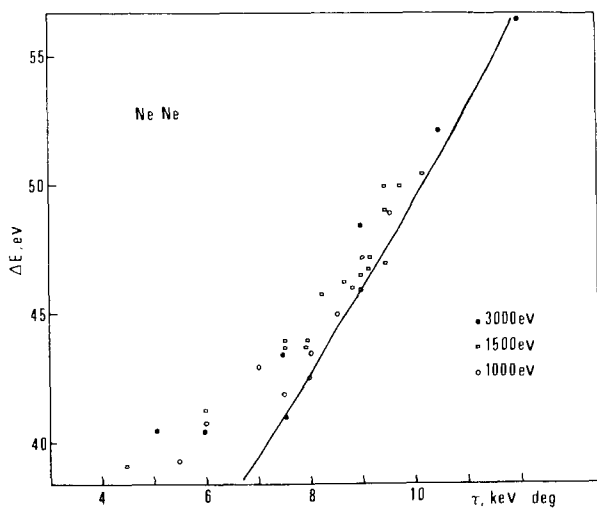
Potential energy curves, difference potentials and electron spectra obtained at two collision temperatures (350K and 900K) for the He(2^1S) + Ar system.

We will now examine experimental results obtained with a differential analysis of the final state of the collisions. They are energy-loss spectra of the ion coming out of the collision at a given angle; by energy conservation they correspond to the energy spectrum of the ejected electrons.

He^+-He collisions (Gillen et al. 1977, Phys. Rev., 15, 527). Various ionizing processes are observed in the 100 eV range. One of these processes, labelled B has its maximum changing with the angle θ and the collision energy E . However, the position of the maximum is only a function of the reduced angle $\tau = E\theta$. It is interpreted as the maximum ionization taking place at the turning point of the trajectory. The curve-labelled theory is just the position of the turning point.

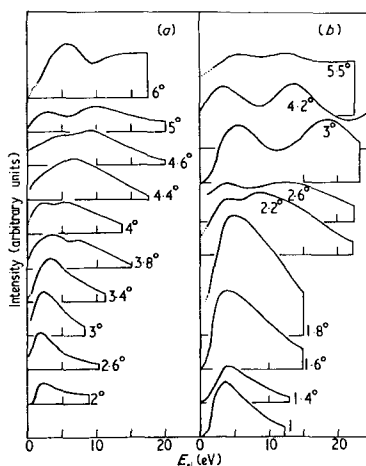


Same kind of effect for Ne-Ne collisions (Brenot et al. 1975, Phys.Rev.A 11, 1245) $\text{Ne} + \text{Ne} \rightarrow \text{Ne}^+ + \text{Ne}^* + e^-$. The following figure gives the energy loss of the maximum of the ionization peak in Ne-Ne collisions as a function of the reduced angle. The full line is a theoretical result obtained as the position of the turning point.

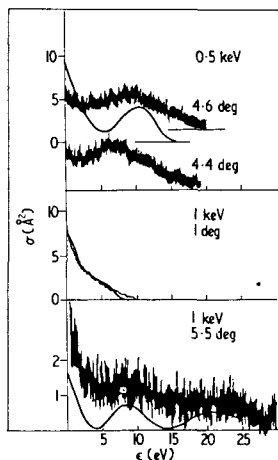


He⁺He system (Barat et al. 1972, J.Phys.B 5, 1343 and Sidis 1973, J.Phys.B 6, 1188)

The energy spectra of He⁺ ions coming out of the collision exhibit oscillations, rapidly changing with the scattering angles. They are interpreted as interferences between ionization occurring in the way in and out of the collision.



Energy spectra of He⁺ ions, associated with ionization in He⁺-He collisions at (a) 500 eV and (b) 1 keV, at different scattering angles.



Experimental and theoretical (full lines) energy loss spectra for ionizing He^+ -He collisions.

The above examples indeed confirm the validity of the qualitative predictions of the LCP approximation. However, one must notice that all the above examples correspond to ionization process via two electron interactions, and this is a very favourable circumstance. Indeed, the states ϕ_d and ϕ_e are rather easy to define in that case and furthermore the width is rather small (for example it amounts to 0.1 eV, for electron energies in the 5-10 eV range, in the He^+ -He case discussed above). It must be noted that all the peculiarities of the electron spectrum studied above are direct consequences of the local character of the decay process: all of them originate from the ϕ_e continuum state being only populated at the point where $E_e = E_d$. The observation of these peculiarities thus mainly confirms the local

Before looking at the detachment problem, we will first go a little backwards and study more in details the states ϕ_ϵ , i.e., look at the problem of one electron scattered by a potential. And since negative ions are mainly concerned with low-energy electrons, we will examine the problem of threshold laws.

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CHAPTER 2

Continuum states - Scattering by a potential

Notation

The Schrödinger equation for scattering by a potential $V(\vec{r})$ is:

$$\left[-\frac{1}{2m} \Delta + V(\vec{r}) \right] \psi = E \psi \quad (1)$$

If $V(\vec{r})$ has a spherical symmetry ($V(\vec{r}) \equiv V(r)$), then the angular part of ψ is a spherical harmonic

$$\psi = \frac{u_l(r)}{r} Y_{lm} \quad \text{for the } l, m \text{ angular mode}$$

and the equation for $u(r)$ is

$$\left[-\frac{1}{2m} \frac{d^2}{dr^2} + \underbrace{V(r) + \frac{l(l+1)}{2mr^2}}_{\text{effective potential}} \right] u_l = E u_l(r) = \frac{k^2}{2m} u_l(r) \quad (2)$$

For $V=0$ potential, the solutions are Bessel functions, regular and irregular. When $r \rightarrow \infty$, for short range potentials, all the potential terms vanish and $u(r)$ becomes a linear combination of sine and cosine functions

$$u_l(r) \xrightarrow{r \rightarrow \infty} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

↖ phase shift

The scattering amplitude is given by

$$f(\theta) = \frac{1}{2ik} \sum_l (2l+1) (e^{2i\delta_l} - 1) P_l(\cos\theta) \quad (3)$$

and the total cross section:

$$(4) \quad \sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \delta_l$$

The asymptotic behaviour of the $u(r)$ function can be expressed in a different way using the scattering S matrix. At larger r , one can express the solution (2) as a linear combination of e^{ikr} and e^{-ikr} exponentials:

$$u_l \xrightarrow{r \rightarrow \infty} A e^{ikr} + B e^{-ikr} \quad (5)$$

The scattering S matrix for the angular momentum l is defined as:

$$S_l = (-1)^{l+1} \frac{A}{B} \quad (5bis)$$

By identification this implies that

$$S_l = e^{2i\delta_l}$$

and

$$S_l = 2ikf_l + 1$$

Threshold laws for short-range potentials

We will examine the k dependence of the scattering properties when $k \rightarrow 0$. The radial Schrödinger equation is:

$$\left[\frac{\delta^2}{\delta r^2} + (k^2 - \frac{1(1+1)}{r^2} - 2mV(r)) \right] u(r) = 0. \quad (6)$$

The method consists in examining the solution of this equation in various regions and matching them.

If $r > a$, range of the potential and $r < 1/k$ wavelength, then only the centrifugal term will be retained in (6)

$$\left[\frac{\delta^2}{\delta r^2} - \frac{1(1+1)}{r^2} \right] u = 0.$$

The solution is then

$$u = \alpha r^{1+1} + \beta r^{-1} \quad (7)$$

The α and β coefficients can be determined by matching this wave function with the solution in the region $r < a$. In this region, one can neglect the energy k^2 and (6) becomes:

$$\left[\frac{\delta^2}{\delta r^2} - \frac{1(1+1)}{r^2} - 2mV(r) \right] u = 0.$$

This equation is independent of the collision energy, and thus when matching its solution with (7), one will get α and β coefficients independent of the energy. (Note that the wave function at this point is not yet normalized; normalization will bring in an energy dependence of α and β , but will keep their ratio independent of the

energy.)

Now if we examine the region $r \gg 1/k$, only the potential can be neglected:

$$\left[\frac{\delta^2}{\delta r^2} + k^2 - \frac{l(l+1)}{r^2} \right] u(r) = 0$$

i.e., the zero potential case. u is then the combination of regular and irregular Bessel functions that joins the wave function (7). This is very easy, since r^{l+1} and r^{-l} are just proportional to the Bessel function for $r \rightarrow 0$. One can then directly derive the asymptotic behaviour of u :

$$u \xrightarrow{r \rightarrow \infty} \frac{\alpha(2l+1)!!}{k^{l+1}} \sin(kr - \frac{l\pi}{2}) + \frac{\beta k^l}{(2l-1)!!} \cos(kr - \frac{l\pi}{2}) \quad (8)$$

From this one gets:

$$\tan \delta_l \approx \delta_l \approx \frac{\alpha}{\beta} \frac{k^{2l+1}}{(2l-1)!!(2l+1)!!} \quad (9)$$

This leads to the threshold law for the phase shifts in the case of short-range potentials

$$\delta_l \propto k^{2l+1} \quad (10)$$

In the determination of total cross sections, the various l terms vary like k^{4l} , and thus at low energies, only the lowest partial waves (and even only the s wave) participate to the scattering. Higher waves cannot penetrate the rotational barrier of the effective potential and are thus kept out of the potential region.

Threshold law for interactions

We will look for the energy variation at threshold of interaction terms like $\langle \phi_d | H_{e1} | \phi_e \rangle$ which appears in the Fermi golden rule. The function ϕ_d of the quasi bound state is localized in space, and to get the threshold law, one can set $\phi_d = 0$ in the region $r \gg a$ where the potential for the ϕ_e scattering vanishes. ϕ_e is one of the u functions studied above, however, it has first to be normalized.

If ϕ_e is energy normalized, its asymptotic behaviour is proportional to:

$$\phi_e \sim \frac{1}{\sqrt{k}} \sin(kr + \frac{1\pi}{2} + \delta_1) = \frac{1}{\sqrt{k}} \{ \cos \delta_1 \sin(kr + \frac{1\pi}{2}) + \sin \delta_1 \cos(kr + \frac{1\pi}{2}) \}$$

when $k \rightarrow 0$,

$$\delta_1 \sim Ak^{2l+1}$$

with A given by (9). Thus

$$\phi_e \sim \frac{1}{\sqrt{k}} \{ \sin(kr + \frac{1\pi}{2}) + Ak^{2l+1} \cos(kr + \frac{1\pi}{2}) \}.$$

By identification with (8), one finds that ϕ_e is equal to the product of u (formula 8, energy independent in the region $r \leq a$) by $k^{l+(1/2)/\alpha(2l+1)!!}$

Thus in the inner region ($r \lesssim a$), the energy normalized function ϕ_ϵ will depend upon the energy only by a multiplicative factor $k^{1+1/2}$ and the threshold law for the interaction is

$$\langle \phi_d | H_{el} | \phi_\epsilon \rangle \propto k^{1+1/2}$$

and for the corresponding width:

$$\Gamma(\text{Fermi}) \propto \epsilon^{1+1/2} \quad (11)$$

The strong energy dependence of the width corresponds to the fact that in order to escape, the electron has to tunnel through the rotational barrier. The transmission of this barrier indeed decreases with the energy of the electron, and with increasing l values.

For s wave problem, the width Γ starts at threshold like $\sqrt{\epsilon}$, i.e., with an infinite slope. Indeed, there is no rotational barrier in that case and nothing to trap the electron. Then as soon as the system becomes unstable, it becomes highly unstable. This is at variance with the $l > 0$ case, where the width is very small at threshold. Another consequence of this sharp energy dependence of the interaction concerns the possibility of application of the LCP: since the LCP requires slowly varying coupling terms, it will break down at threshold.

Threshold laws for the amplitude:

The scattering amplitude is:

$$f_l = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{\sin\delta_l}{-i\delta_l} = \frac{1}{k \cot\delta_l - ik} = f_l \quad (12)$$

The threshold law for the phase shift is $\delta_l = \alpha k^{2l+1}$ Thus

$$\cot\delta_l \simeq \frac{1}{\delta_l} = \alpha^{-1} k^{-2l-1}$$

and

$$k \cot\delta_l \simeq \alpha^{-1} k^{-2l}$$

s-wave: then $k \cot\delta$ is a constant χ at low energies

$$f_l \simeq \frac{1}{\chi - ik} \quad \text{and} \quad \sigma = \frac{4\pi}{\chi^2 + k^2} \quad (13)$$

The cross section goes to a constant at zero energy. If χ^2 is very small, then the cross section has a sharp maximum for zero energy. In this case, the scattering amplitude has a pole for an imaginary value of k :

$$k = -i\chi.$$

A pole of the scattering amplitude is also a pole of the S matrix and this corresponds (via (5)) to the existence of a solution of the Schrödinger equation with a pure outgoing wave behaviour at infinity (e^{ikr}).