

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_{e1} , 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_{e1} which are solutions of the electronic problem

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:

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

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

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

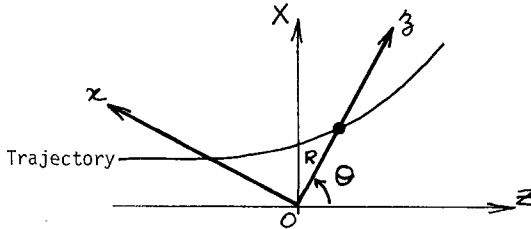
with the following boundary condition: $|c_i(-\infty)|^2$ vanishing except for the initial state of the collision, where it amounts to one. One has then the following picture; the system is travelling along the potential energy curves $E_i(R)$ of the various ϕ_i^{el} states with a probability amplitude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

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

(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:

$$\theta_{e1, Oxyz} = \theta_{e1, OXYZ} - \theta$$

electronic angular variables around Oy, OY

Thus,

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

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

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

The coupled equations are then:

$$i \frac{dc_i}{dt} = E_i c_i(t) + \sum_j c_j(t) \langle \phi_i^{el} | H_{el} | \phi_j^{el} \rangle$$

$$+ \sum_j (-i \frac{dR}{dt}) \langle \phi_i^{el} | \frac{\delta}{\delta R} | \phi_j^{el} \rangle c_j(t) \quad (9)$$

$$+ \sum_j (-\frac{d\theta}{dt}) \langle \phi_i^{el} | L_y | \phi_j^{el} \rangle c_j(t)$$

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 Γ 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_ϵ 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_ϵ by the electronic Hamiltonian. The continuum states are assumed to be uncoupled. The coupled equations (9) are:

$$\begin{aligned} i \frac{dc}{dt} &= E_d c(t) + \int d\epsilon \langle \phi_d | H_{el} | \phi_\epsilon \rangle C_\epsilon(t) \\ i \frac{dC_\epsilon}{dt} &= E_\epsilon C_\epsilon(t) + \langle \phi_\epsilon | H_{el} | \phi_d \rangle c(t). \end{aligned} \quad (10)$$

With the following change of function:

$$\begin{aligned} b(t) &= \exp(-i \int_{t_0}^t E_d dt') c(t) \\ b_\epsilon(t) &= \exp(-i \int_{t_0}^t E_\epsilon dt') C_\epsilon(t). \end{aligned}$$

The second equation becomes

$$i \frac{db_\epsilon}{dt} = \langle \phi_\epsilon | H_{el} | \phi_d \rangle e^{-i \int_{t_0}^t (E_d - E_\epsilon) dt'} b(t).$$

When brought into the first equation, it yields:

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

with the notation $\langle \phi_\epsilon | H_{el} | \phi_d \rangle = V_{\epsilon d}(t)$ (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:

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

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

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

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

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 $E_d(t')$

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

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

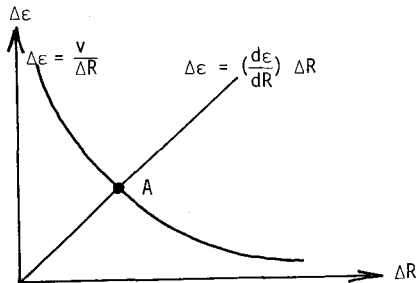
$$\frac{db}{dt} = -\pi |V_{dE_d}(t)|^2 b(t) \quad (13)$$

Thus the localization appears through the relation $E_\varepsilon = E_d(t)$. 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_ϵ and their couplings can be defined;
- $V_{d\epsilon}(t)$ 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_e can be defined
- $V_{de}(t)$ 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 $\phi_d \phi_e$ 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

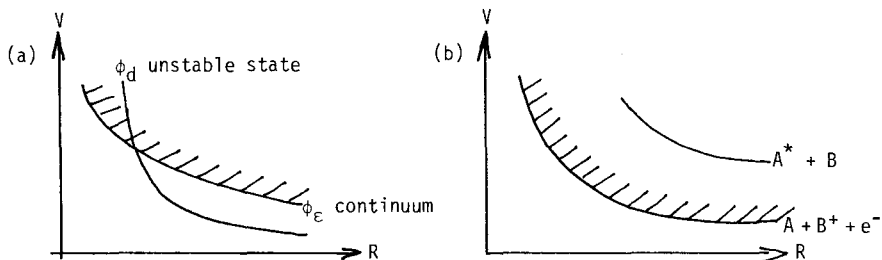
- Attempts to treat the non local decay rate: Wang and Delos 1984,
Phys.Rev.A 29 542

- 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

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:

$$dP_{\text{ion}} = dP_{\text{ion}}^{\text{in}} + dP_{\text{ion}}^{\text{out}} = \frac{\Gamma(R)}{v_R} dR e^{-\int_R^{\infty} \Gamma \frac{dR}{v_R}} [1 + e^{-\int_{R_0}^R 2\Gamma \frac{dR}{v_R}}]$$

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

$$Sp(\epsilon) = \frac{dP_{\text{ion}}}{dR} \frac{dR}{d\epsilon} = \frac{dR}{d\epsilon} \frac{\Gamma}{v_R} e^{-\int_R^{\infty} \Gamma \frac{dR}{v_R}} [1 + e^{-2\int_{R_0}^R \Gamma \frac{dR}{v_R}}] \quad (18)$$

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):

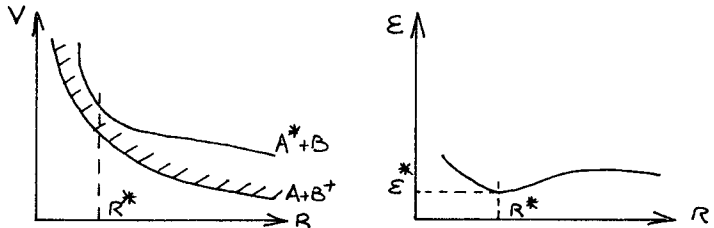
- At the classical turning point of the trajectory R_0 , the radial velocity vanishes, and that causes a divergence of the spectrum $Sp(\epsilon)$. However, if one considers the integral of $Sp(\epsilon)$ like in (17):

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

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 :

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

↑
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.

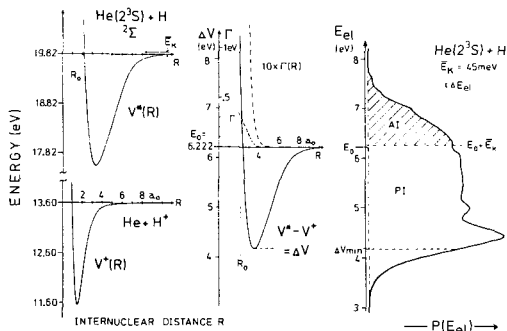
We will now examine a few experimental results which exhibit the various features detailed above. First we will consider results for the Penning ionization in He metastable H and Ar collisions. (The examples are taken from an invited talk by H.Hotop at the XI ICPEAC in Kyoto 1979; book page 271). They 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.

He(2^3S)H system

Potential energy curves
of the system

Energy difference
 $\epsilon(R)$

Energy spectrum
of ejected electrons
 $E_K = 45 \text{ meV}$
collision



$V^*(R)$ is the potential energy curve of $\text{He}^* - \text{H}$

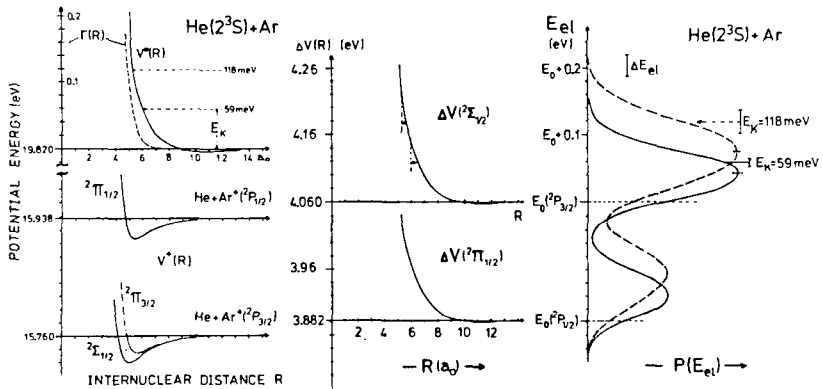
$V^+(R)$ " " " " $\text{H}^+ - \text{He}$

The energy difference $\epsilon = V^* - V^+$ presents an extremum around 4.1 eV, which is visible in the energy spectrum of ejected electrons.

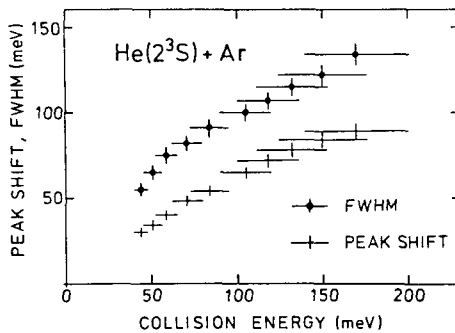
An interesting point is the boundary between the Penning ionization region (PI) and the associative ionization (AI) region: the spectrum is continuous over the boundary.

He(2^3S)-Ar system

The energy difference is monotonic. The spectrum for ejected electrons changes with the collision energy, moving to higher electron energy when the collision energy is increased, since the system can go higher on the $\epsilon(R)$ curve. Two exit channels are present corresponding to the two fine-structure levels of Ar^+ , thus yielding two $\epsilon(R)$ functions.



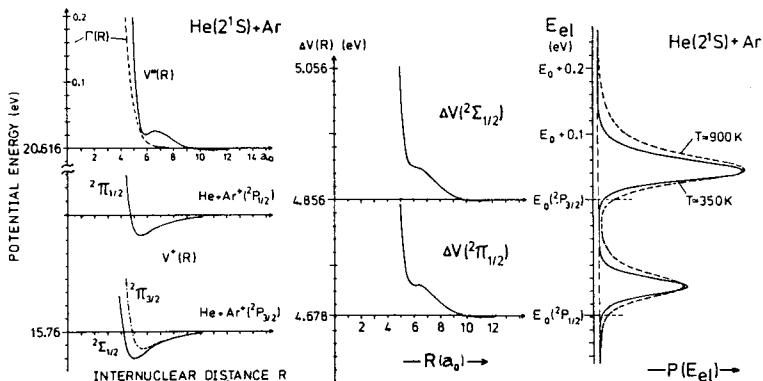
Potential energy curves, difference potentials, and electron spectra at the two collision energies of 59 meV and 118 meV for $\text{He}(2^3\text{S}) + \text{Ar}$



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

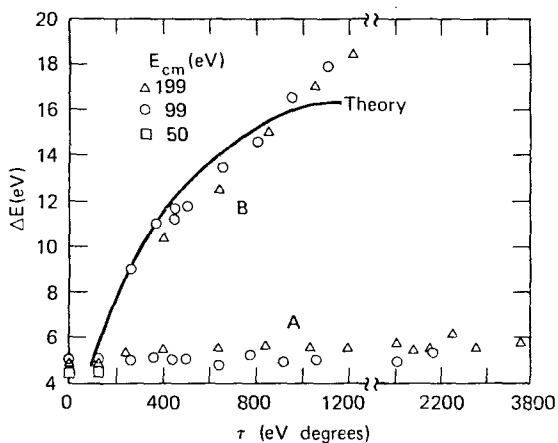
Two exit channels ($\text{Ar}^+ 2^2P_{3/2}, 2^2P_{1/2}$) are present, and in both of them the $\epsilon(R)$ function exhibits a shoulder. It results in a peak in the electron energy spectrum which does not move when the collision energy changes.



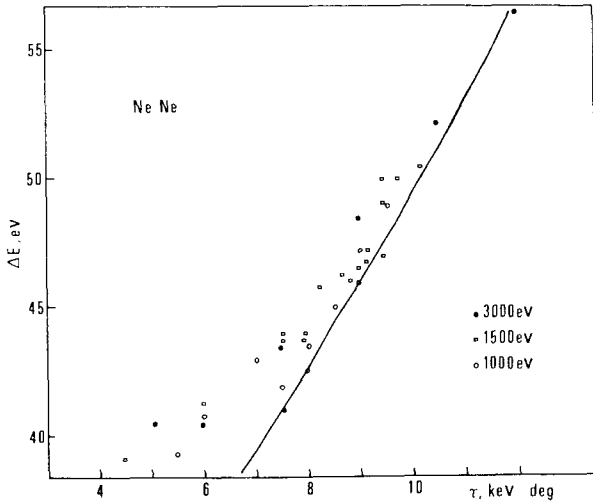
Potential energy curves, difference potentials and electron spectra obtained at two collision temperatures (350K and 900K) for the He(2^1S) + Ar system.

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.

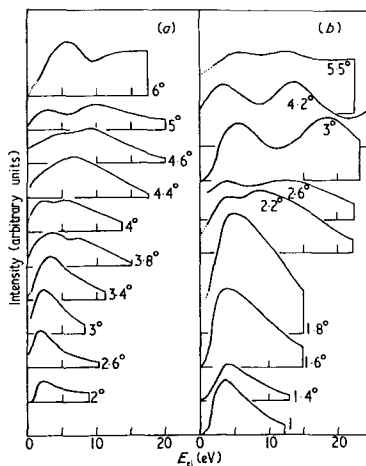


Same kind of effect for Ne-Ne collisions (Brenot et al.1975, Phys.Rev.A 11, 1245) $\text{Ne} + \text{Ne} \rightarrow \text{Ne}^+ + \text{Ne}^{*+} + e^-$. The following figure gives the energy loss of the maximum of the ionization peak in Ne-Ne collisions as a function of the reduced angle. The full line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

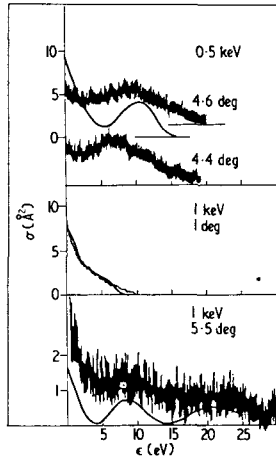


He⁺He system (Barat et al. 1972, J.Phys.B 5, 1343 and Sidis 1973, J.Phys.B 6, 1188)

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

character of the bound-free transitions in these systems. The case of negative ions is rather different. As already said, detachment is often a one-electron problem and thus the definition of ϕ_d and ϕ_e is not obvious. The one-electron interactions are also more important and very easily lead to very large widths (10 eV range). For those reasons, the LCP approximation was very early recognized to fail for detachment problems.

Before looking at the detachment problem, we will first go a little backwards and study more in details the states ϕ_e , 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.

Bibliography to chapter 1:

- The analysis of the time evolution of the population of a constant quasistationary state interacting with a continuum can be found in many quantum mechanics text books, e.g., in COHEN-TANNOUJDI C., DIU B., and LALOE F. 1977 "Mecanique Quantique", Hermann, Paris.

- The problem of a constant quasi stationary state interacting with a continuum can also be studied as a static problem, using the energy as a variable with a configuration interaction technique: FANO U. 1961, Phys.Rev.124, 1866

- Derivations of the local complex potential method can be found in the following papers:

BARDSLEY J.N. 1968, J.Phys.B 1, 349 (presented in chapter 5)

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