Pathways to charge equilibration following multiple electron exchange between highly charged ions and atoms

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Chapter 2

Overbarrier model

2.1 Introduction

During collisions between highly charged ions and gas targets, target electrons will be affected by the extra Coulomb field carried by the ion. They can be transferred to the ion, depending on several factors. One of the most important quantity is the impact parameter. Capture of electrons will occur with high probability into excited states of the ion. The resulting excited projectile ion will decay to the ground state via photon emission or autoionization. The energy of the emitted electrons or photons after collisions between highly charged ions and gas targets, is a mapping of the initial populated quantum levels and a fingerprint of the underlying electron capture dynamics.

In the following section we will describe a semi-classical electron capture model based on sequential capture of electrons as described by Niehaus (1986). The model describes collisions of type:

$$A^{q+} + B \rightarrow A^{(q-t)+} + B^{t+}$$

with A the q-fold charged ion, and B the target, whereby t electrons are transferred.

In section 2.2 this model will shortly be explained. The predictions of initially populated orbitals can be tested by measuring the energy distributions of photons and electrons.

2.2 The overbarrier model (OVB)

The binding energy of an electron i in the target B is denoted with E_i, where i ranges between 1 and N with N the total number of electrons in the atom. The most loosely bound electron has index 1, the most strongly bound one index N. For hydrogen-like ions the binding energy of electrons in a level n is given by:

$$E = \frac{q^2}{2n^2} \tag{2.1}$$

(Atomic units are used throughout this thesis. An overview of the different units can be found at the end of this thesis.)

The binding energies of electrons in ions with more than one electron can be calculated using quantum-mechanical calculations, like self-consistent Hartree-Fock calculations (Cowan 1981).

The electron binding energy in the target is shifted due to the charge of the projectile. A semi-classical description will be given in the next section 2.2.1. To predict the quantum levels into which electrons are captured during the collision, also the collision velocity should be taken into account. In section 2.2.2 this will be discussed.

2.2.1 Resonant electron transfer

When an ion approaches an atom, the binding energy of an electron i is increased due to the external field of the ion according to:

$$I_i(R) = E_i + \frac{q}{R} \tag{2.2}$$

where R is the internuclear distance. The potential seen by electron i is the potential of the approaching ion added to that of its own nucleus:

$$V_i(r) = \frac{q}{|r|} + \frac{i}{|(R-r)|} \tag{2.3}$$

In figure 2.1 as an example $V_1(r)$ is plotted for C^{6+}-Ar. The height of the potential barrier depends on the internuclear distance. The maximum of the barrier at distance $r_{i,max}$ for an electron i can be deduced from the derivative of eq. 2.3.

This yields for the maximum between the two nuclei:

$$\frac{dV}{dr} = -\frac{q}{r^2} + \frac{i}{(R-r)^2} = 0 \tag{2.4}$$

so $r_{i,max}$ is:

$$r_{i,max} = R(1 + \sqrt{\frac{i}{q}})^{-1} = \frac{R\sqrt{q}}{\sqrt{q} + \sqrt{i}} \tag{2.5}$$

Inserting this result into eq. 2.3 leads to the following expression for the barrier height $V_{i,max}$ seen by an electron i:

$$V_{i,max} = \frac{q}{R} + \frac{1}{R}(i + 2\sqrt{iq}) \tag{2.6}$$

The distance R_i at which the electron can transit from the target to the ion, i.e. the distance at which $V_{i,max}$ (2.6) equals the shifted binding energy of electron i (2.2), is calculated to be:

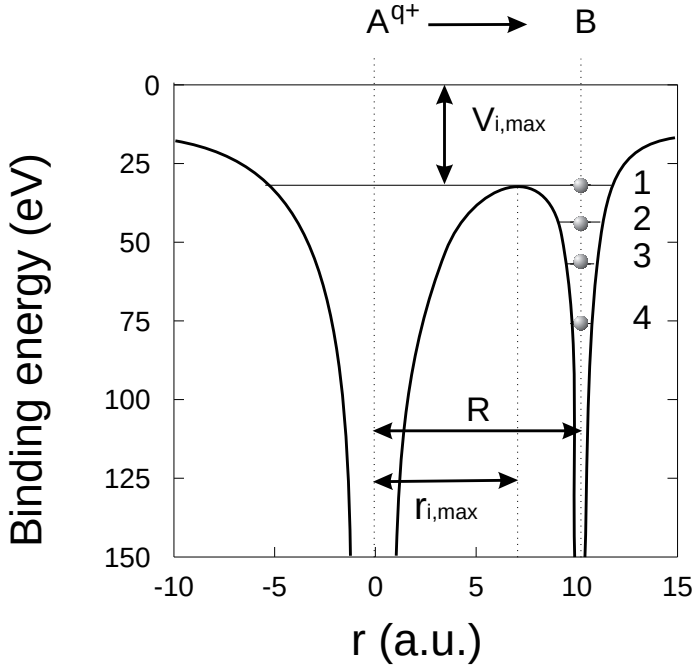

Figure 2.1: Definitions of the different parameters used in the overbarrier model.

$$R_i = \frac{i + 2\sqrt{iq}}{E_i} \tag{2.7}$$

In the overbarrier model it is assumed that on the way-in of the collision, i.e. when the collision partners are approaching, the shifted binding energy I_i^{qm} remains fixed for internuclear distances smaller than R_i, i.e. for $r \leq R_i$

$$I_i^{qm} \equiv I_i(R_i) = E_i + \frac{q}{R_i} \tag{2.8}$$

On the way-in electrons become subsequently quasi-molecular until the distance of closest approach is reached. From then on the potential barrier increases again. At the point on the way-out where the potential barrier between the ions equals the binding energy of the quasi-molecular electron, the electron has to 'choose' whether it will be captured by the ion or recaptured by the target. Such a sequence is depicted in figure 2.2. In figure 2.2a the potential seen by the most loosely bound electron is sketched for the case that the collision partners are separated such that the maximum of the barrier equals the binding energy of this electron. At this point the electron becomes quasi-molecular. In figure 2.2b the height of the potential barrier equals the shifted binding energy of the third electron. The two previous electrons are in a quasi-molecular state. On the way-out of the collision at a certain moment the potential barrier reaches the

binding energy of e.g. the third electron (figure 2.2c). The electron chooses at this point whether it is captured or recaptured. Note that in the situation depicted in figure 2.2c the fourth electron is recaptured during the collision, the third is captured but the first two electrons are still in a molecular state.

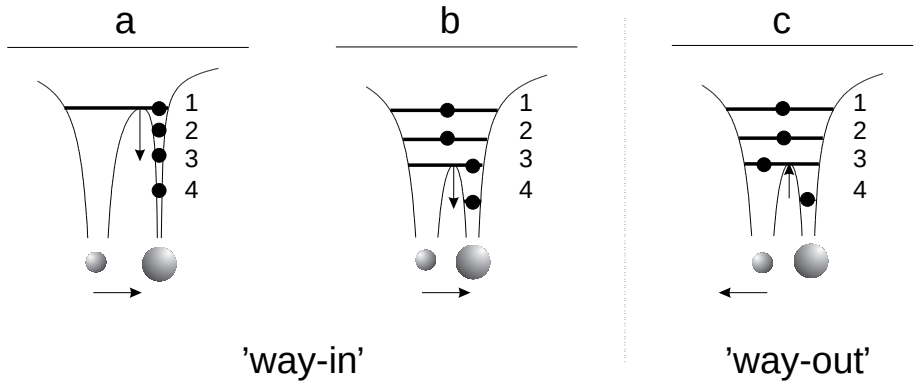

Figure 2.2: On the way-in the barrier between the electrons decreases and sequentially the electrons become quasi-molecular. In (a) the system is plotted at the distance where the first electron becomes quasi-molecular. In (b) the third electron becomes molecular. On the way-out the electrons have to decide if they are captured or recaptured. In (c) this situation is plotted for the third electron.

Each capture or recapture process has an influence on the charges seen by the next electron. Depending on what happened this next electron will be captured or recaptured at a certain distance. This procedure is repeated until the most loosely bound electron looses its quasi-molecular character. The binding energy of the electrons is dependent on the exact redistribution of the previously captured electrons.

The potential experienced by an electron i is thus dependent on the number of already captured electrons c_i. As a consequence the potential V_i^o at internuclear distance R on the way-out will be:

$$V_i^o = \frac{q - c_i}{|r|} + \frac{i + c_i}{|R - r|} \tag{2.9}$$

Taking the derivative leads to the following expression for the maximum of the potential barrier $V_{i,max}^o$:

$$V_{i,max}^o = \frac{q}{R} + \frac{1}{R}(i + 2\sqrt{(i + c_i)}\sqrt{(q - c_i)}) \tag{2.10}$$

The distance $R_{i,max}^o$ corresponding to the place where the height of the potential energy is equal to the quasi-molecular binding energy (eq. 2.8) of electron i is

$$R^o_{i,max} = R_{i,max}\left(\frac{\sqrt{q-c_i}+\sqrt{i+c_i}}{\sqrt{q}+\sqrt{i}}\right)^2 \tag{2.11}$$

Due to the change in effective charge seen by the electron the binding energy will also change. At infinite internuclear separation this yields the binding energy I^o_i

$$I^o_i = E_i + \frac{q}{R_i} - \frac{i+c_i}{R^o_i} \tag{2.12}$$

The binding energy I^o_i is assumed to be the effective binding energy of the electron to the ion-core. It is also assumed that captured electrons effectively screen the core to which they are captured.

The electron capture process can be characterized using so called *strings*. A sequence of '1' and '0' indicate the capture or recapture of an electron, respectively. For example: the string {110} indicates the process where the impact parameter is such that a maximum of three electrons become quasi-molecular during the collision. Read from left to right it indicates that the most loosely bound electron is captured, the second electron is captured too, and the third electron is *re*captured by the target.

In table 2.1 an example for the collision of C^{6+}- Ar is depicted. Tabulated are: the string, the distances of capture and recapture and the effective binding energies of electrons during and after the collision.

electron nr	1	2	3	4	5	6
string	{1	1	1	0	0	1 }
E_i (eV)	15.7	27.6	40.9	59.8	75.0	91.0
$R_{i,max}(au)$	10.2	8.80	7.68	6.23	5.79	5.38
$R^o_{i,max}(au)$	11.9	9.43	7.88	6.34	5.79	5.38
I_i^{qm} (eV)	31.8	46.2	61.9	85.8	103	121
I^o_i (eV)	22.6	34.6	48.2	64.4	79.7	91.0

Table 2.1: An example of calculations using the overbarrier model for collisions between C^{6+} and Ar. The calculations are for the string {111001} where six electrons become quasi-molecular, but only the first three as well as the last electron are captured.

In this example six electrons become quasi-molecular, i.e. the impact parameter is between R_6 and R_7 (4.4 a.u.). The electron transfer calculations are for the string {111001}. During the collision one by one the electrons become quasi-molecular, but on the way-out the sixth electron is captured by the projectile, the fifth and fourth electron are recaptured by the target and the third, second and first electron are captured by the projectile. This leads to a two-fold ionized projectile and a four-fold charged target.

An important remark can be made here regarding the meaning of strings with different 'length'. As an example, the string {11100} and {111} yield the same

binding energies and transfer radii of the captured electrons. But the important difference between these two are the actual impact parameters. Electron capture for the first string takes place at much smaller impact parameters compared to the last one. This distinction plays a role in the final state distribution which is described in the next section.

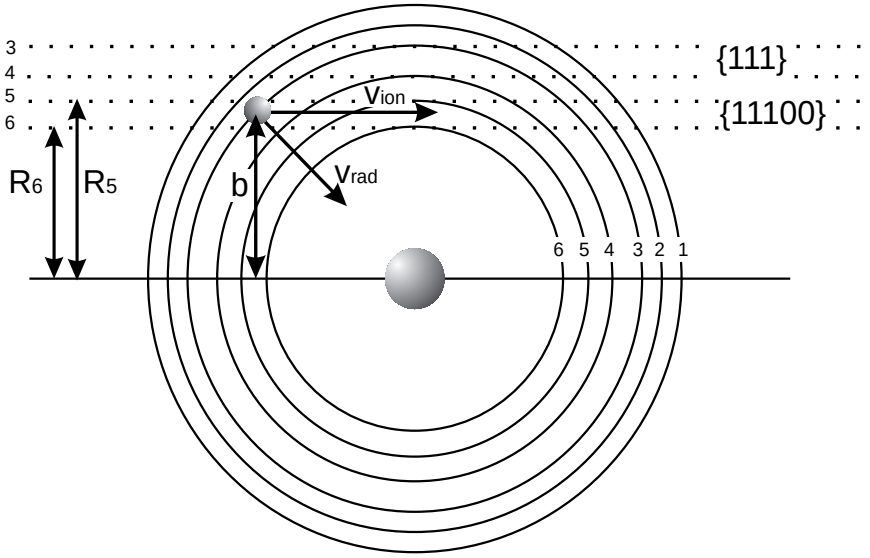

Figure 2.3: The main difference between the strings {111} and {11100} is the range of relevant impact parameters b. For the latter string five electrons become quasi-molecular: $R_6 < b < R_5$, yielding a geometrical cross-section $\sigma_{geo} = \pi(R_5^2 - R_6^2)$. For the first string σ_{geo} equals $\sigma_{geo} = \pi(R_3^2 - R_4^2)$. For both strings also the radial velocity $v_{rad}(R)$ is different.

2.2.2 The extended overbarrier model

So far no collision energy dependence is taken into account. Also no predictions are made of the quantum levels in which the electrons are actually captured. The latter can be dealt with if a hydrogenic approximation is used. Rewriting equation 2.1 and assuming that the calculated binding energy I_i^o for electron i corresponds to "classical" principal a quantum number n_i^d, which is given by:

$$n_i^d = \frac{q - c_i}{\sqrt{2I_i^o}} \tag{2.13}$$

In general these are non-integer numbers. To project these classical numbers to the integer quantum number n the following inequality is often used (Olson 1982):

$$\{(n-1)(n-\frac{1}{2})n\}^{\frac{1}{3}} < n_i^d < \{n(n+\frac{1}{2})(n+1)\}^{\frac{1}{3}} \tag{2.14}$$

A velocity dependence follows when one realizes that the raise of the barrier is velocity dependent. The change of the potential with time can be expressed as

$$\frac{dV}{dt} = \frac{dV}{dR}\frac{dR}{dt} \tag{2.15}$$

or rather:

$$\Delta V = \frac{dV}{dt}\Delta t = \frac{dV}{dR}\frac{dR}{dt}\Delta t \tag{2.16}$$

The term $\frac{dR}{dt} = v_b^r$ is the radial velocity and $\frac{dV}{dR}$ the derivative of eq. 2.6.

At $R = R_{i,max}$ and $R = R^o_{i,max}$, the distance at which the maximum of the potential barrier equals the binding energy of electron on the way-in and way-out respectively, dV/dR is found to be:

$$\frac{dV}{dR}|_{R_i} = \left(\frac{\sqrt{q}+\sqrt{i}}{R_{i,max}}\right)^2 \tag{2.17}$$

and

$$\frac{dV}{dR}|_{R_i^o} = \left(\frac{\sqrt{q-c_i}+\sqrt{i+c_i}}{R^o_{i,max}}\right)^2 \tag{2.18}$$

respectively.

For each string the average radial velocity term $\frac{dR}{dt}$ can be calculated. In figure 2.3 an example is plotted for an ion passing the target at a certain impact parameter b. The indicated radii are the distances at which electrons become quasi-molecular. The average value of the radial velocity can be calculated by averaging over all radial velocities v^i_{rad}.

$$\overline{v}^i_{rad} = \frac{\int_{R_{t+1}}^{R_t} v^i_{rad} b db}{\int_{R_{t+1}}^{R_t} b db} \tag{2.19}$$

in which R_t and R_{t+1} are the upper and lower limits of the impact parameter and v^i_{rad} given by the radial part of the projectile ion velocity.

The uncertainty relation in energy and time $\Delta V \Delta t \sim 1$ combined with equation 2.16 leads to a minimum uncertainty ΔV_{min}:

$$\Delta V_{min} = \sqrt{|\frac{dV}{dR}\frac{dR}{dt}|} = \sqrt{|\frac{dV}{dR}\overline{v}^i_{rad}|} \tag{2.20}$$

The total uncertainty or width ΔV_i in binding energy for electron i depends on the width on the way-in and on the way-out. Assuming a Gaussian distribution around the calculated binding energy I_i^o (eq 2.12) this gives

$$\Delta V_i = \sqrt{(\Delta V_{min})^2 + (\Delta V^o_{min})^2} \tag{2.21}$$

The distribution formed by the Gaussian is called the 'reaction window'. The reaction window provides the range of final binding energies. The square of the

total width of the reaction window, corresponding to a complete string, can be calculated by summing the squares of the separate widths of each electron.

The cross section σ for a certain string is

$$\sigma = \sigma_{geo} \times \prod_{i}^{s} W_i \tag{2.22}$$

where s the number of electrons in a string and W_i is the probability to capture or recapture electron i, maintaining the string characteristic. An approximation of the probability W_i is the ratio between the number of states available in the projectile with respect to the total number of available orbitals for capture and recapture of electrons. Quantum mechanically the degeneracy of a certain hydrogenic level n is $2n^2$ thus assuming that for a certain non-integer n_i this also holds and leads to the probability W_i of capture of an electron:

$$W_i = \frac{n_i^2}{n_i^2 + m_i^2} \tag{2.23}$$

The classical quantum number is indicated by n_i for capture and m_i for recapture of electron i. The area of the reaction window is now assumed to be proportional to the calculated cross section.

2.3 Summary

The overbarrier model is a semi-classical model to describe the capture of electrons by highly charged ions from atomic gas targets. It provides predictions on binding energies of captured or recaptured electrons, reaction windows and cross-sections. The reaction can be described using 'strings', i.e. a sequence of '1' and '0' containing information on the reaction characteristic. Throughout this thesis the validity of the model is tested. A remark can be made here. Except for the charge state the model does not incorporate any dependence on the core structure of the projectile ion. This assumption holds to explain the gross features of the collisional dynamics. However, in chapter 6 it is shown that it is important to include the structure of the projectile ion.

The information obtained with the overbarrier model can serve to interpret the gross features of experimental results from collisions between highly charged ions and gas targets.

References

Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (University of California Press, Berkley, 1981)
Niehaus A 1986 *J. Phys. B: At. Mol. Phys.* **19** 2925
Olson R E 1981 *Phys. Rev. A* **24** 1726