Cometary X-rays
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Charge exchange is a process in which one or more electrons are transferred from one particle to another, and it is the dominant reaction between ions and neutrals up to collision velocities of several hundreds of kilometers per second. The net reaction is:

\[ A^{q+} + B \rightarrow A^{(q-r)+} + B^{(r+s)+} + se^- \tag{3.1} \]

Here \( A \) is an ion with charge \( q \), that captures \( r \) electrons from an initially neutral target \( B \). This target is left with a charge \( r + s \) as \( s \) electrons are lost to the continuum. The dominant reaction channel in most charge transfer reactions is single electron capture (SEC), where one electron is captured from the target into an excited state of the projectile ion, i.e. \((r, s) = (1, 0)\). The excited state subsequently decays to the ground state by the emission of one or more photons. As will be demonstrated in the experimental chapters of this thesis, multiple-electron processes can be an important reaction channel in collisions between highly charged ions and molecules. An important reaction channel is double capture with \((r, s) = (2, 0)\), where two electrons are captured by the projectile. This can lead to the population of doubly excited states, which most likely decay by the emission of an Auger-electron (auto-ionizing double capture, A2C), or which can radiatively stabilize (bound double capture, B2C). Note that the A2C reaction leads to \((r, s) = (1, 1)\).

The probability \( P \) that charge exchange occurs when an ion traverses through a gas is generally expressed in terms of the cross sections \( \sigma_j \) of the different charge exchange processes:

\[ P = \sum_j \sigma_j \int dr n(r) \tag{3.2} \]

where the integral is taken along the path of the ion through a gas with number density \( n(r) \). The cross sections are typically in the order of \(10^{-16} - 10^{-14} \text{ cm}^2\), depending on the gas and ion combination.

### 3.1 Bohr-Lindhard Model

A first classical description of one electron capture was proposed by Bohr and Lindhard (1954). It is based on classical relations between the forces and energies of the collision
system. Two critical distances are introduced for an ion approaching a neutral target. At the first distance, $R_1$, the coulomb force from the charge $q$ of the projectile attracting the electron is equal to the binding force in the neutral target:\(^1\):

$$\frac{q}{R_1^2} = \frac{2I_b}{a} \quad (3.3)$$

$$R_1 = \sqrt{\frac{aq}{2I_b}} = \frac{\sqrt{aq}}{v_e} \quad (3.4)$$

where $v_e$ is the orbital velocity, $I_b$ the binding energy and $a$ the orbital radius of the target electron. The electron can be captured by the projectile when in the projectile frame, its potential energy is larger than its kinetic energy. This occurs when target and projectile get within the second critical distance $R_2$:

$$\frac{q}{R_2} = \frac{1}{2}v^2 \quad \text{hence} \quad R_2 = \frac{2q}{v^2} \quad (3.5)$$

---

\(^1\)Throughout this chapter, atomic units are used for convenience. See Appendix A for their definition and conversion.
where \( v \) is the collision velocity of the projectile. When \( R_1 < R_2 \), the electron is immediately captured when it is released and the geometrical electron capture cross section is given by:

\[
\sigma = \pi R_1^2 = \pi \frac{aq}{2I_b}
\]

Note that this implies that for velocities below the critical velocity \( v_c \), given by:

\[
v_c = \left( \frac{8I_b q}{a} \right) \frac{1}{4}
\]

the cross section is independent of the projectile velocity, but that for higher velocities, \( R_1 > R_2 \) - the electron is released before it can be captured by the projectile. If the release process would occur instantaneously, electron capture would be impossible and the cross section would become zero. However, the release takes a finite amount of time and occurs with a probability of \( v_e/a \) per unit time. Therefore, there is a chance that the electron is still not released when the projectile is within the capture distance \( R_2 \). The probability of electron release within a distance \( R_2 \) is determined by the product of the release probability per unit time \( (v_e/a) \) and the time during which capture can take place \( (R_2/v) \). Thus for \( R_1 > R_2 \), the electron capture cross section is given by:

\[
\sigma = \pi R_2^2 \left( \frac{v_e}{a} \cdot \frac{R_2}{v} \right) = 8\sqrt{2} \pi q^3 \sqrt{I_b} a^{-1} v^{-7}
\]

At velocities below \( v_c \), the Bohr-Lindhard model thus predicts cross sections that are dependent on the charge of the projectile and the binding energy of the target, but not of the collision velocity. Above velocities \( v_c \), the cross section decreases strongly with increasing velocity.

Resulting charge exchange cross sections for capture from atomic hydrogen by projectiles with increasing charge are shown in Fig. 3.1. For the orbital radius \( a \), expectation values of the radial probability density are used, using hydrogenic wavefunctions with an effective nuclear charge \( Z_{\text{eff}} \):

\[
<1/r>^{-1} = n^2 / Z_{\text{eff}}
\]

With a maximum acceleration voltage of 24 kV (see Chapter 4), all collisions discussed in this thesis fall within the low velocity regime of the Bohr-Lindhard model.

### 3.2 Classical Over-the-Barrier Model

The Classical Over-the-Barrier model (CoB) is a comprehensible approximation for collisions between ions and neutrals at energies in the range of 100 eV/amu up to 10 keV/amu. It allows for estimates of electron capture cross sections, and the principal quantum number \( n \) into which the electron is captured. The CoB model describes reactions of the type:

\[
A^{q+} + B \rightarrow A^{*(q-r)+} + B^{r+}
\]

where \( A^{q+} \) is the projectile ion with charge \( q \), which captures \( r \) electrons from a neutral target \( B \).
The model is based on the idea that if the projectile approaches a target close enough, the electron can freely move in their joint potential well, called a quasi-molecular state. This occurs when the height of the potential barrier between the two nuclei is lower than the binding energy of the target electron. At an infinite separation \( R = \infty \), the neutral’s least bound electron has a (negative) binding energy \( I_\text{b} \). The approaching ion’s Coulomb field causes a Stark shift which increases the electron’s binding energy:

\[
I_\text{b}(R) = I_\text{b}(\infty) - \frac{q}{R}
\]

where \( R \) is the internuclear distance. The full potential experienced by an electron at a distance \( r \) of the target nucleus is the sum of the potential of the ion and that of the target:

\[
V(r) = -\frac{q}{|R-r|} - \frac{1}{|r|} \quad \text{for} \quad 0 < |r| < |R|
\]

The top of the barrier is reached for exactly that \( r \) where the derivative of this equation equals zero. Solving this equality yields both the position \( r_{\text{max}} \) and the magnitude \( V_{\text{max}} \) of the top of the potential barrier:

\[
\frac{dV(r)}{dr} = -\frac{q}{(R-r)^2} + \frac{1}{r^2} = 0
\]

\[
r_{\text{max}} = \frac{R}{\sqrt{|q|} + 1}
\]

\[
V_{\text{max}} = -\frac{q}{R} - \frac{1 + 2\sqrt{|q|}}{R} = -\frac{(\sqrt{|q|} + 1)^2}{R}
\]

The electron can escape from the target when \( V_{\text{max}} \) becomes smaller than the binding energy of the electron:

\[
-\frac{q}{R} - \frac{1 + 2\sqrt{|q|}}{R} = I_\text{b}(\infty) - \frac{q}{R}
\]

which yields a capture distance \( R_c \) at which charge exchange can occur:

\[
R_c = \frac{2\sqrt{|q|} + 1}{-I_\text{b}(\infty)}
\]

From this distance, the cross section for the one electron capture process can be determined by assuming that if ions pass the neutral at a distance smaller than this critical distance \( R_c \), the electron is captured with unit probability. The electron capture cross section is then given by the geometrical cross section, weighted with the capture probability \( A \):

\[
\sigma = \pi R_c^2 = \pi \left( \frac{2\sqrt{|q|} + 1}{I_\text{b}(\infty)} \right)^2
\]

A value of \( A = 0.5 \) has been determined from both theory (Baede, 1975) and experiments (Dijkkamp et al., 1985).

In the CoB, it is assumed that during the quasi-molecular state, the binding energy of the electron remains fixed. On the way out, the potential barrier starts to increase again.
Figure 3.2: Classical Over-the-Barrier predictions for collisions between ions with charge $q$ and $H_2O$ molecules. Top panel: Capture cross sections. Bottom panel: ‘Classical’ principal quantum number $n_{cl}$ into which the electron is likely to be captured.
The binding energy $I_f$ of the captured electron at infinitive $R$ equals its energy at the barrier crossing, lowered by the Stark shift induced by the (now charged) target:

$$I_f = I_b(R_c) + \frac{1}{R_c} = I_b - \frac{q - 1}{R_c}$$

(3.19)

Electron capture thus results in an increase of the binding energy of the captured electron. This binding energy can be used to predict the state $n$ into which the electron is most likely to be captured. This can be done by converting the binding energy $I_f$ into a ‘classical’ energy level $n_{cl}$ by the hydrogenic approximation:

$$n_{cl} = \frac{q}{\sqrt{2I_f}}$$

(3.20)

Although the Classical Over-the-Barrier model does not give an exact distribution over the $n$-states, the availability of states near the predicted binding energies may give information on the effectiveness of certain electron capture processes. If the decimal fraction of $n_{cl}$ is between 0.5 – 0.8 the actual $n$ distribution strongly depends on the collision energy.

COB predictions for ions typical for the solar wind colliding on a H$_2$O molecule are shown in Fig. 3.2. The principal quantum number into which the electron the electron is captured increases steadily with increasing projectile charge $q$, from $n = 1 – 7$ for $q = 1 – 10$. The cross section increase approximately linear with the projectile charge and ranges from $18 – 110 \times 10^{-16}$ cm$^2$ for projectiles with $q = 1 – 10$.

As an example of the COB, consider the collision of O$^{7+}$ + H$_2$O, which is described experimentally in Chapter 7. A cartoon of the COB interaction of this system is shown in Fig. 3.3. Initially, the electron is bound in the target molecule with $I_b = 12.6$ eV. At an internuclear distance of $R_c = 13.6$ a.u. (7.2 Å), the electron can cross the potential barrier. This capture distance is equivalent to a capture cross section of $81 \times 10^{-16}$ cm$^2$. Its binding energy at the capture distance is $I_b(R_c) = 26.6$ eV. Upon separation, the final binding energy of the electron in the projectile $I_f = 24.6$ eV. Following Eq. 3.20, this results in $n = 5.2$. The most likely principal quantum shell into which the electron is captured is thus the $n = 5$ state.

### 3.2.1 Multiple Electron Capture

Analogue to single electron capture in the previous section, the COB model can also be applied to multiple electron capture processes (Ryufuku et al., 1980; Niehaus, 1986). When the projectile ion approaches the neutral target, the electrons subsequently enter the quasi-molecular state. The potential experienced by the $i^{th}$ electron is:

$$V_i^{in}(r) = \frac{q}{|R - r|} - \frac{i}{|r|}$$

(3.21)

resulting in a transit distance for the $i^{th}$ electron given by:

$$R_i^{in} = \frac{i + 2\sqrt{iq}}{-I_{b,i}(\infty)}$$

(3.22)
3.2 Classical Over-the-Barrier Model

![Graph showing the Over-the-Barrier model](image)

Figure 3.3: The Over-the-Barrier model for an O\(^{7+}\) ion colliding on a neutral H\(_2\)O molecule. **Upper left panel:** The ion approaches the water molecule. When the ion approaches the molecule, the potential barrier between the two is lowered. **Upper right panel:** At a distance of \(R_{in}=13.6\) a.u. (\(\sim 7.2\) Å), the potential barrier becomes lower than the binding energy of the outermost electron of the target. **Lower left panel:** The electron is in a quasi-molecular state. **Lower right panel:** On the way out, at a distance of \(R_{out}=13.6\) a.u. (\(\sim 7.2\) Å), the quasi-molecular electron is either captured by the projectile ion or recaptured by the target molecule.

where \(I_{b,i}(\infty)\) is the binding energy of the \(i^{th}\) target electron at infinite internuclear separation. On the way out, these electrons are assumed to be sequentially captured by the projectile, or recaptured by the target. As in the one electron model, these capture processes occur at the distance where the potential barrier equals the binding energy of the quasi-molecular electron \(I_{b,i}(R_{in}^{in})\):

\[
R_{i}^{out} = R_{i}^{in} \left( \frac{\sqrt{q-j+i+c}}{\sqrt{q+i}} \right)^2
\]

(3.23)

where \(c\) is the number of already captured electrons at the moment of capture of the \(i^{th}\) electron (by either projectile or target). If the electron is captured by the projectile, its final
binding energy at infinite internuclear separation is:

$$I_{f,i} = I_{b,i}(\infty) - \frac{q}{R_i^{in}} + \frac{i + c}{R_i^{out}} = I_{b,i}(\infty)\left(1 + \delta(q, i, c)\right)$$ (3.24)

where \(\delta(q, i, c)\) is defined as:

$$\delta(q, i, c) \equiv \frac{1}{i + 2\sqrt{qi}} \left(q - \left(\frac{\sqrt{q} + \sqrt{i}}{1 + \sqrt{\frac{q-c}{i+c}}}\right)^2\right)$$ (3.25)

The geometrical cross sections for capture of the \(i^{th}\) electron capture is now a shell, delimited by the transit distances of the \(i^{th}\) and the next \((i + 1)^{th}\) electron, weighted by the capture probability \(A_i\):

$$\sigma_i = A_i \pi \left((R_i^{in})^2 - (R_i^{in+1})^2\right)$$ (3.26)

To illustrate this, consider a two electron process for \(O^{7+}\) colliding on \(H_2O\). The first electron still becomes quasi-molecular at 13.6 a.u. Using a vertical double ionization energy of 41 eV (Alvarado et al., 2005) for the \(H_2O\) molecule yields \(R_i^{in} = 9.6\) a.u. On the way out, the 2nd electron is captured first (at 9.6 a.u.) and will be bound with a binding energy of 41.2 eV. The other electron is captured at \(R_i^{out} = 15.3\) a.u., and bound with 23.1 eV. Note that this is slightly less than in the one electron case, as a result of the larger Stark shift of the ionized target. The geometric cross section for one electron capture is \(41 \times 10^{-16}\) cm\(^2\), and for double electron capture \(40 \times 10^{-16}\) cm\(^2\). Based on the CoB model, it is to be expected that for collision between \(O^{7+}\) and \(H_2O\), bound double capture is as likely as single electron capture.

### 3.2.2 Reaction Window

The discussion above assumes that an electron is captured resonantly; the detailed inner structure of the projectile is considered to match the binding energy of the electron(s) from the target perfectly. In practice, this is not the case.

There is an uncertainty in the binding energy due to the finite time \(\Delta t\) an electron needs to cross the potential barrier. If this time interval is short, the uncertainty in the binding energy is determined by the Heisenberg uncertainty principle. For longer time intervals, the uncertainty is given by the change barrier height. In this way, the Extended Over-the-Barrier model predicts a Gaussian distribution of binding energies around the most probable final binding energy, called the reaction window. The distribution around the final binding energy for an electron \(i\) is assumed to be a Gaussian distribution with a standard deviation given by:

$$\Delta I_{f,i} = \sqrt{0.5 \cdot ((\Delta V_i^{in})^2 + (\Delta V_i^{out})^2)}$$ (3.27)

The assumption is made that this classical uncertainty in the barrier height is equal to the quantum mechanical uncertainty

$$\Delta V \Delta t \sim 1$$ (3.28)
3.2 Classical Over-the-Barrier Model

The radial velocity $v_{rad}$ of the projectile, i.e. the component of the projectile velocity along the internuclear axis, determines how fast the potential barrier will raise in the finite time $\Delta t$ it takes an electron to cross the barrier results in an uncertainty in the barrier height $\Delta V$, which can be expressed as:

$$\Delta V = \frac{dV}{dR} \cdot v_{rad} \cdot \Delta t$$

(3.29)

so that a minimum uncertainty is given by:

$$(\Delta V)^2 = \frac{dV}{dR} \cdot v_{rad}$$

(3.30)

For simplicity, we will consider here an interaction system in which only the outer two electrons are involved. Both on the way in and on the way out, there is an internuclear distance $R$ at which the height of the potential barrier is equal to the shifted binding energy. Substitution of these distances gives:

$$\left. \frac{dV_i}{dR} \right|_{R_i^{in}} = \left( \frac{\sqrt{q} + \sqrt{i}}{R_i^{in}} \right)^2$$

(3.31)

$$\left. \frac{dV_i}{dR} \right|_{R_i^{out}} = \left( \frac{\sqrt{q} - \sqrt{i}}{R_i^{out}} \right)^2$$

(3.32)

The radial velocity $v_{rad}$ is related to the projectile velocity $v_p$ and the impact parameter $b$ by:

$$v_{rad} = v_0 \cdot \sqrt{1 - \left( \frac{b}{R_i} \right)^2}$$

(3.33)

Niehaus (1986) originally used the radial velocity at the smallest impact parameter possible for the considered electron capture process. Hoekstra et al. (1991) however proposed to use the radial velocity averaged over all internuclear distances for which the electrons can cross the potential barrier, which is a more accurate approach. In that way the average velocities at $R_i^{in}$ and $R_i^{out}$ are found to be:

$$\bar{v}_{rad,i}^{\text{in}} = \frac{2}{3} v_p \left( \frac{R_i^{in}}{R_{i+1}^{in}} \right)^2 \left\{ 1 - \left( 1 - \left( \frac{R_{i+1}^{in}}{R_{i}^{in}} \right)^2 \right)^{\frac{3}{2}} \right\}$$

(3.34)

$$\bar{v}_{rad,i}^{\text{out}} = \frac{2}{3} v_p \left( \frac{R_i^{out}}{R_{i+1}^{in}} \right)^2 \left\{ 1 - \left( 1 - \left( \frac{R_{i+1}^{out}}{R_{i}^{out}} \right)^2 \right)^{\frac{3}{2}} \right\}$$

(3.35)

The reaction window can now be expressed as:

$$W_i(E) = \frac{1}{\sqrt{\pi} \cdot \Delta I_{f,i}} \exp \left( - \left( \frac{E + I_{f,i}}{\Delta I_{f,i}} \right)^2 \right)$$

(3.36)
Figure 3.4: Widening of the reaction window with increasing velocity, for single electron capture by O\textsuperscript{7+} from a H\textsubscript{2}O molecule. Velocities of 0.2, 1.0 and 10 keV/amu were used and the position of the excited OVII n-shells are indicated.

The reaction window can be used to roughly predict the distribution of final states of the ion that are populated by considering the overlap between the reaction window and the binding energies of the final ionic states. The reaction window widens as the velocity increases with a $v^{1/2}$ dependence so that for larger velocities, more states can be populated.

This is illustrated in Fig. 3.4 for one electron capture by O\textsuperscript{7+} from H\textsubscript{2}O. Capture occurs almost resonantly into the $n = 5$ channel. At higher collision energies however, the reaction window widens and capture into $n = 6$ also becomes possible. These findings are indeed confirmed by experiments described in Chapter 7.