Chapter 2

Theoretical Models

2.1 Introduction

A full quantum-mechanical non-relativistic treatment of collisions between ionic and atomic particles, leading to charge transfer and ionization processes, relies on solving of the time-dependent Schrödinger equation for a given initial state:

\[ i \frac{\partial \Psi(t)}{\partial t} = H \Psi(t), \quad \Psi(t_0) = \Psi_0, \quad (2.1) \]

where the Hamiltonian \( H = T + V \) takes into account the kinetic and potential energies of all particles. The probability of finding the system after the collision in state \( f \), represented by the wave function \( \psi_f(t) \), can be determined from the projection of the total wave function \( \Psi(t) \) on this state, i.e.

\[ c_f = \lim_{t \to \infty} \langle \psi_f(t) | \Psi(t) \rangle, \quad (2.2) \]

at time \( t \) long after the collision at which the particles do not interact anymore. The probability is given by \( |c_f|^2 \). However, such an \textit{ab initio} approach is in practice impossible, even for the most simple one-electron systems, and approximate methods have to be used.

As a first step one can separate the nuclear and electronic dynamics, the so-called ‘semi-classical approximation’ in which the electronic motion is treated quantum mechanically and the nuclear motion classically. The validity of this approximation can be shown by considering the wavelength associated with the motion of the heavy projectile. The de Broglie wavelength \( \lambda \) of a particle of mass \( M \) and velocity \( v \) is given by:

\[ \lambda = \frac{1}{Mv}, \quad (2.3) \]

For protons having a kinetic energy of 1 eV, which corresponds to a velocity of \( 10^4 \) m/s, this leads to \( \lambda \approx 0.1 \) a.u., which is small compared with the distance over which the interaction takes place, namely 1-100 a.u. Therefore the motion of the projectile ion can be considered

\[ ^1 \text{Atomic units are used throughout this thesis, i.e. } \hbar = m_e = e = 4\pi \varepsilon_0 = 1, \text{ see appendix A.} \]
Theoretical Models

as a classical trajectory for energies larger than 1 eV/amu. Furthermore, curved trajectories with non constant projectile velocities have to be considered only at impact energies well below 1 keV/amu. For higher energies the nuclear motion $R(t)$ can be taken as a straight-line classical trajectory, i.e. $R(t) = R(b, 0, v_p t)$, where $b$ is the impact parameter and $v_p$ is the projectile velocity.

The first application of quantum mechanics to charge exchange in ion-atom collisions was the perturbation treatment by Oppenheimer [28] and by Brinkman and Kramer [29]. They derived that the first order perturbation approximation of the transition amplitude has the form,

$$e_f^{OBK} = -i \int_{-\infty}^{+\infty} \langle \psi_f(t) | V(t) | \Psi_0 \rangle .$$

which is now known as the Oppenheimer-Brinkman-Kramer (OBK) approximation. However, at impact energies $< 50$ keV/amu electron capture cross sections are large and perturbation methods are not appropriate. At these energies the relative velocity of the heavy particles is comparable to or smaller than the orbital velocities of the target electrons, resulting in long interaction times on the electronic time-scale. During the collision the electrons can be shared between the projectile and the target, forming a quasi-molecule during part of the interaction. As the two heavy-particles separate, the probabilities of capture by the projectile or of remaining at the target are comparable.

The first non-perturbative theory has been presented by Massey and Smith [30] and was based on the expansion of the electronic wave function in a series of molecular orbitals. Due to the required computing power the application of the method was only possible much later. By now these so-called ‘close-coupling’ or ‘coupled channel’ calculations, based on a finite basis set expansion of atomic or molecular orbitals, provide the most extensively applied quantum-mechanical description of charge transfer and ionization processes in low energy ion-atom collisions. A detailed and extensive overview of several theoretical methods can be found in [31].

Despite the feasibility of quantum-mechanical descriptions also classical models are considered to gain general insight into the transition mechanisms and dependencies on the collision parameters. A theoretical model based on classical mechanics was constructed by Thomas [32]. The capture of a bound electron by a fast projectile was described as a double scattering event whereby the electron is first scattered off the projectile and then scattered elastically off the target nucleus. An electron which finally moves with the same velocity and in the same direction as the projectile is considered to be captured. This model predicts a velocity dependence of $v_p^{-11}$ of the cross section. The Thomas scattering mechanism was observed experimentally by Horsdal-Pedersen et al [33] and Vogt et al [34] but generally plays only a minor role.

A simple classical model valid for one-electron capture in a broad energy range (keV to MeV) was introduced by Bohr and Lindhard [35] and later elaborated by Knudsen et al [36]. Here an electron can only be transferred if the Coulomb force exerted by the projectile exceeds the initial binding force and if the electron’s kinetic energy in the projectile frame is smaller than its potential energy. The model predicts an energy independent cross section at low impact energies. At high energies the cross section decreases as $v_p^{-7}$, in good agreement with experimental data [36].

Interest in multiple electron capture processes lead to the classical over-barrier model,
mainly developed by Ryufuku et al [37], Mann et al [38], Bárány et al [39] and Niehaus [40]. This model is based on the idea that electrons can transit from the target to the projectile at internuclear distances at which the height of the potential barrier between the two nuclei is lower than the Stark shifted binding energy of the electrons. Multi-electron capture cross sections as well as final state distributions are predicted.

A completely classical description is provided by the classical trajectory Monte Carlo method. Here the Hamilton’s equations of motion are solved numerically for all particles while the Coulomb interactions between all of them are included. These calculations have proven to be very useful for the study of (multi-) electron capture and (multiple-) ionization processes in keV ion-atom collisions.

In this chapter theoretical models applicable to keV ion-atom collisions are discussed. First of all two analytical solutions of the quantum-mechanical two-state model are discussed, namely the Demkov model and Landau-Zener model. Then the classical approaches according to the Bohr-Lindhard model and the classical over-barrier model are treated. Finally, the close-coupling basis generator method and the classical trajectory Monte Carlo method will be described.

### 2.2 Two-state quantum-mechanical models

Transitions between two electronic states representing the initial bound state at the target and the final state at the projectile can be well treated by starting from the Schrödinger equation (equation 2.1). One speaks of adiabatic conditions if the collision is slow enough such that the electronic system follows the variations of the atomic field. It means that there is a set of wave functions $\psi_i$ for each internuclear distance $R$, which are eigenfunctions of the Schrödinger equation:

$$H \psi_i(r, R) = \varepsilon_i(R) \psi_i(r, R).$$

where $r$ represents the electronic coordinates. The wave functions $\psi_i$ represent the adiabatic basis and can be seen as quasi-molecular states. The total electronic wave function of the system has the form

$$\Psi(r, R, t) = \sum_i c_i(t) \psi_i(r, R) \exp \left(-i \int_0^t \varepsilon_i(t') dt' \right).$$

The probability of a transition from the initial state $\psi_0 = \Psi(t \to -\infty)$ to a final state $\psi_j$ is then given by $P_j = |c_j(+\infty)|^2$, and an expression can be obtained by inserting the total wave function into the Schrödinger equation.

To assess whether a transition between two non-degenerate states is likely to occur one can use the so-called the Massey adiabatic criterion

$$\frac{\Delta \epsilon a}{v_p} \simeq 1,$$

where $a$ is the typical interaction range, $\Delta \epsilon = |\varepsilon_0 - \varepsilon_j|$ is the energy spacing between the two levels, and $v_p$ is the projectile velocity [41]. The Massey criterion is a manifestation of the Heisenberg uncertainty principle. The electronic energy in the collision is defined only to
within $\Delta \varepsilon \sim 1/\Delta t$, where $\Delta t = a/v_p$ is the time of interaction. Transitions to states within this energy are probable but transitions to other states are unlikely to happen. Because the energies of the electronic states can change with internuclear distance, $\Delta \varepsilon$ is not necessarily equal to the energy difference at infinite separation ($R \to \infty$). From the velocity dependence of the Massey criterion an estimate can be made of the impact energies at which non-resonant charge transfer processes become important. For energy differences on the order of a few eV and a typical interaction range of $\sim 10$ a.u., collision energies of about 10 keV/amu are sufficient to induce transitions. This explains why non-resonant transitions in ion-atom collisions become important in the keV energy range.

To investigate non-resonant transitions a basis of stationary wave functions will be used (diabatic basis). This means that the wave functions $\psi_1$ and $\psi_2$ are orthonormal eigenstates of the unperturbed Hamiltonian $H_0$. The total wave function can be represented in the form

$$\Psi(t) = (c_1(t)\psi_1 + c_2(t)\psi_2) \exp \left[ -\frac{i}{2} \int_t^{t'} (H_{11} + H_{22}) dt' \right],$$

(2.8)

where $H_{ij} = \langle \psi_i | H | \psi_j \rangle$. By substituting the diabatic expansion into the Schrödinger equation (equation 2.1) one can obtain the following set of equations for the probability amplitudes,

$$i \frac{dc_1}{dt} = (1/2) \Delta V c_1 + H_{12} c_2,$$

$$i \frac{dc_2}{dt} = H_{12} c_1 - (1/2) \Delta V c_2,$$

(2.9)

where $\Delta V(R) = H_{11} - H_{22}$ represents the energy difference between the potential energy curves of state 1 and 2. $H_{12}$ is the coupling-matrix element, describing the coupling between the two states. As initial condition at $t \to -\infty$ we take $c_1 = 1$ and $c_2 = 0$, and the transition probability for a transfer from state 1 to 2 is given as $P = |c_2(+\infty)|^2$.

The solution of equations 2.9 is determined by the time dependence of the parameters $\Delta V$ and $H_{12}$ (via their dependence on the internuclear distance $R$). The equations cannot be solved analytically for any arbitrary form of $\Delta V$ and $H_{12}$. In the following we will discuss two cases which have an analytic solution, namely one in which the energy difference between the states is constant while the coupling term depends exponentially on the internuclear distance (Demkov model), and one in which the energy difference depends linearly on time and crosses zero while the coupling term remains constant (Landau-Zener model). The first case corresponds to strongly interacting close lying parallel potential energy curves, while the second case is related to well localized transitions at (avoided) curve crossings.

### 2.2.1 Demkov Model

The Demkov model has been developed particularly to describe the systems with a near-degeneracy at $R \to \infty$ and no strong curve crossing at a finite value of $R$ [42]. For alkali targets it has been successfully applied to one-electron capture in asymmetric alkali-ion–alkali-atom collision systems at $E < 5$ keV/amu [43].

To solve the set of equations 2.9 the following Ansatz is used for the potential curve difference and coupling-matrix element:

$$\Delta V = \text{constant}, \quad H_{12} = e^{-\lambda R}.$$

(2.10)
Figure 2.1: Demkov calculations of potential curve difference $|\Delta V|$ (—) and the coupling-matrix element $2H_{12}$ (—) for the $H^+ + Na(3s)\rightarrow H(n=2) + Na^+$ (left panel) and $He^{2+} + Na(3s)\rightarrow He^+ (n=3) + Na^+$ transition (right panel).

The transition probability as a function of impact parameter $b$ is calculated to be:

$$P(b) = \text{sech}^2\left(\frac{\pi |\Delta V|}{2\lambda v_{\text{rad}}}\right) \sin^2\left(\int_{-\infty}^{\infty} H_{12} dt\right),$$

(2.11)

which is the Demkov formula, where $v_{\text{rad}} = v_p \sqrt{1 - (b/R)^2}$ is the radial velocity, i.e. the component of the projectile velocity $v_p$ along the internuclear axis. Averaging over the phase, i.e. $\sin^2\left(\int_{-\infty}^{\infty} H_{12} dt\right) = 1/2$, leads to:

$$P(b) = \frac{1}{2} \text{sech}^2\left(\frac{\pi |\Delta V|}{2\lambda v_{\text{rad}}}\right),$$

(2.12)

which is the Rosen-Zener formula. The transition probability maximizes at an internuclear distance $R_c$ where the difference between the potential curves equals twice the coupling-matrix element, i.e.,

$$H_{12}(R_c) = \frac{1}{2} |H_{11}(R_c) - H_{22}(R_c)| = \frac{1}{2} |\Delta V|.$$  

(2.13)

The simple exponential form of the coupling-matrix element and the constancy of $\Delta V$ need only to be valid in the region around $R_c$. Olson proposed the following generic expression for the coupling-matrix element [44]:

$$H_{12}(R) = \sqrt{I_1 I_2} R^* e^{-0.86 R^*},$$

(2.14)

where $I_i$ is the ionization potential of state $i$ ($i = 1, 2$) and $R^* = \frac{1}{2} \left(\sqrt{2I_1} + \sqrt{2I_2}\right) R$, which corresponds to $\lambda = 0.43 \left(\sqrt{2I_1} + \sqrt{2I_2}\right)$. The difference between the potential curves can be approximated by (neglecting polarization effects):

$$\Delta V(R) = I_1 - I_2 + \frac{q - 1}{R},$$

(2.15)
where $q$ is the projectile charge state. For singly charged ion–atom collisions the last term vanishes. Using equations 2.14 and 2.15 one can determine $R_c$ after which $P(b)$ can be calculated. The cross section is obtained by integrating $P(b)$ over the relevant impact parameter range, i.e.,

$$\sigma = 2\pi \int_0^{b_{\text{max}}} bP(b)db.$$  

(2.16)

In order to examine the applicability of this model to the collision systems studied here $|\Delta V|$ and $2H_{12}$ for the main charge transfer channels in $H^+$ and $He^{2+}$ collisions on Na(3$s$) are plotted in figure 2.1. $R_c$ is determined by $|\Delta V| = 2H_{12}$. For $H^+$ a crossing at 5.7 a.u. is calculated. For $He^{2+}$ the Demkov model is not applicable because there is no effective crossing. We observe the same behavior for projectiles with higher charge states.

The Demkov cross section for the $H^+ + Na(3s) \rightarrow H(n=2) + Na^+$ reaction is shown in figure 2.2a, together with the present data and recent calculations (see chapter 5). It shows that for $E < 10$ keV/amu the model underestimates the cross section considerably. The overestimation at high impact energy might be due to the omission of capture to other channels (mainly $n \geq 3$) and ionization, which contributes significantly to electron removal at the cost of capture into $n=2$.

The same calculations have also been performed on a system which is considered to be well described by the Demkov model, namely $Li^+ + Na(3s) \rightarrow Li(2s) + Na^+$, and the result is shown in figure 2.2b, together with close-coupling calculations [45] (see section 2.5). For $E < 5$ keV/amu reasonable agreement is found. It is of note that the binding energy difference between Na(3$s$) and Li(2$s$) is only 0.25 eV, much smaller than the typical transition energies in the collision systems studied in this thesis.
2.2.2 Landau-Zener Model

The Landau-Zener (LZ) model [46, 47] has been developed specifically to deal with curve crossings at finite $R$. Such crossings occur in collision systems involving highly charged ions because of the very different nature of initial and final potential curves, e.g., an attractive polarization potential between ions and neutral atoms in the initial channel and a strong repulsive Coulomb potential between the two ions in the final electron capture channel. The LZ model has therefore been extensively applied to charge transfer in collisions between highly charged ions and atomic hydrogen or helium (see e.g. [48–50]).

The LZ model relies on the following Ansatz to solve the set of equations 2.9:

$$\Delta V(t) = \Delta F v_{\text{rad}}(t-t_c), \quad H_{12} = \text{constant},$$

(2.17)

such that $\Delta V$ describes a crossing of the potential energy curves at $t = t_c$, i.e. it is connected to a crossing at internuclear distance $R_c$: $\Delta V \propto R - R_c$. $\Delta F$ is the difference in slopes of the potential energy curves at $R_c$, i.e. $\Delta F = [dH_{11}/dR - dH_{22}/dR]_{R=R_c}$. The transition probability for a single diabatic passage of the crossing region is given by:

$$p = \exp \left( -\frac{2\pi H_{12}^2}{\Delta F v_{\text{rad}}} \right),$$

(2.18)

which is called the Landau-Zener formula. Because the crossing region is passed twice (on the incoming and outgoing trajectory) the overall transition probability is given by:

$$P(b) = 2p(1 - p).$$

(2.19)

Estimating the crossing radius $R_c$ by assuming a pure Coulomb curve for the outgoing channel and a constant curve for the incoming channel, yields:

$$\Delta V(R) = I_1 - I_2 + \frac{q - 1}{R} = 0,$$

(2.20)

from which $R_c$ is obtained as,

$$R_c = \frac{q - 1}{Q},$$

(2.21)

where $Q = I_1 - I_2$ is the so-called Q-value of the reaction. Crossings can only occur with states which are stronger bound than the initial state, i.e. $I_2 > I_1$, such that $Q < 0$. In that sense the LZ model is only applicable to exothermic reactions. $\Delta F$ is given by:

$$\Delta F = \frac{q - 1}{R_c^2}.$$

(2.22)

By calculating the potential curves for a large number of ion-atomic hydrogen systems Olson and Salop obtained a general expression for the coupling matrix elements [48]:

$$H_{12} = \frac{9.13}{\sqrt{q}} \exp \left( -\frac{1.324 \alpha R_c}{\sqrt{q}} \right),$$

(2.23)
where \( \alpha = \sqrt{2I} \) takes into account the extension to other targets than H. Note that for atomic hydrogen \( I = 0.5 \) a.u., thus \( \alpha = 1 \). The cross section is finally obtained by integrating \( P(b) \) (equation 2.19) over the impact parameter range \([0, R_c]\) (cf. equation 2.16).

In order to investigate the applicability of the LZ model to our collision systems, one can plot the cross section as function of the Q-value, leading to so-called reaction windows [51]. They are shown in figure 2.3 for one-electron capture in collisions between \( \text{He}^{2+} \) and \( \text{O}^{6+} \) and \( \text{Na}(3s) \) and \( \text{Na}^*(3p) \). The Q-values for specific projectile states are indicated, too. For increasing impact energy the reaction windows broaden and shift towards more negative Q-values. For \( \text{He}^{2+} \) the reaction window falls in between available final levels, which would imply small cross sections. However, experimentally large capture cross section are observed. Therefore the Landau-Zener model does not provide a realistic description as was already pointed out by Schweinzer and Winter [52].

For \( \text{O}^{6+} \) the reaction windows encompass final states of the system. However, the LZ predicts the dominance of capture into a lower \( n \)-shell (\( n = 6 \) for \( \text{Na}(3s) \) and \( n = 7 \) for \( \text{Na}^*(3p) \)) than found experimentally and calculated by close-coupling calculations (\( n = 7 \) and \( n = 9 \), respectively) (see chapter 7 and 8). Extension of the LZ model to many states [50] and the
2.3 Bohr-Lindhard Model

A first classical description of one-electron capture in collisions between highly charged ions and atomic targets was provided by Bohr and Lindhard [35]. It has proven to give good estimations of the absolute cross sections and their dependencies on the impact energy, target electron binding energy and projectile charge state [36].

Two distinctive ion–atom interaction distances are introduced. Firstly the electron can be released from the target nucleus when the projectile is close enough that its attractive Coulomb force is equal to the binding force of the electron in the atom, i.e.,

$$\frac{q}{R^2} = \frac{\nu_e^2}{a},$$  \hfill (2.24)

where $\nu_e$ and $a$ are the velocity of the electron and the radius of its orbital, respectively, as defined in the Bohr model. The release distance $R_r$ is then given by:

$$R_r = \sqrt{\frac{qa}{\nu_e^2}}.$$  \hfill (2.25)

Secondly, the electron can be captured if in the projectile frame its potential energy is larger than its kinetic energy. The distance at which this condition becomes valid is determined by

$$\frac{q}{R} = \frac{1}{2} \nu_p^2,$$  \hfill (2.26)
Theoretical Models

and capture is possible for distances smaller than

\[ R_c = \frac{2q}{v_p^2}, \quad (2.27) \]

which is called the capture distance.

For \( R_r < R_c \) the condition for capture is fulfilled and the cross section is given by

\[ \sigma_{\text{cap}} = \pi R_r^2 = \pi \frac{qa}{v_e^2}. \quad (2.28) \]

This means that for projectile velocities \( v_p < v_{cr} = \sqrt{2v_e (\frac{q}{a})^{1/4}} \), with \( v_{cr} \) the critical velocity defined by \( R_r = R_c \), the capture cross section is independent of the impact energy.

On the other hand for \( R_r > R_c \) release can take place before capture is possible. If the release process would happen instantaneously, capture would not be possible and the cross section would become zero. However, the release takes a finite amount of time while the projectile is passing the target, and takes place only with a probability per unit time of the order of \( v_e/a \). Therefore there is a chance that the electron is still at the target when the internuclear distance has decreased below the capture distance. The probability of electron release within a distance \( R_c \) is on the order of \( (R_c/v_p)(v_e/a) \). Thus for \( R_r > R_c \) the cross section is

\[ \sigma_{\text{cap}} = \pi R_c^2 \left( \frac{v_e R_c}{a v_p} \right) = 8\pi q^3 \frac{v_e}{a} v_p^{-7}, \quad (2.29) \]

meaning that for projectile velocities \( v_p > v_{cr} \) the capture cross section decreases very strongly with increasing projectile velocity as \( v_p^{-7} \). The two cross section regions do not match at \( v_p = v_{cr} \) if the factor \( (R_c/v_p)(v_e/a) \) is not equal to one.

In figure 2.4 Bohr-Lindhard cross sections are shown for one-electron capture from Na(3s) by H\(^+\), He\(^{2+}\) and O\(^{6+}\) projectiles. Also a comparison between capture from Na(3s) and Na\(^+\)(3p) by O\(^{6+}\) is made. The velocity of the target electron \( v_e \) is calculated from the relation with the ionization potential \( I \), namely \( v_e = \sqrt{2I} \). For the orbital radius \( a \) the \( \langle 1/r \rangle^{-1} = n^2/Z_{\text{eff}} \) expectation values of the radial probability densities are taken, using hydrogenic wavefunctions with an effective nuclear charge. This yields for Na(3s) \( a = 4.9 \) a.u. \( (Z_{\text{eff}} = 1.84) \) and for Na\(^+\)(3p) \( a = 6.3 \) a.u. \( (Z_{\text{eff}} = 1.42) \).

Considering single ionization we can already make the observation that according to the Bohr-Lindhard model ionization has a threshold at \( v_p=v_{cr} \), under the assumption that ionization can only occur for \( R < R_r \). For lower velocities capture is 100% efficient because the second condition, \( R_r < R_c \), is always fulfilled. However for higher velocities ionization becomes possible, if we interpret the situation that an electron is released but not captured as an ionization event.

Bohr obtained an analytical expression for the ionization cross section, based on the Rutherford cross section for energy transfer to a free, stationary electron [53, 54]. Ionization occurs when the energy transferred exceeds the ionization potential. Therefore the ionization cross section is obtained by the integration of the Rutherford cross section from the ionization potential \( I \) to the maximum transferable energy \( 2v_p^2 \) and found to be:

\[ \sigma_{\text{ion}} = 4\pi q^2 v_p^{-2}[(2I)^{-1} - (2v_p)^{-2}]. \quad (2.30) \]
Results for Na are plotted in figure 2.5. The energy dependence clearly differs from that of one-electron capture. Here the cross section is zero for low impact velocities, $v_p < (I/2)^{1/2}$, steeply increases to a maximum at $v_p = I^{1/2}$ and finally decreases as $v_p^{-2}$ at higher velocities. Because the capture cross section drops much more rapidly, ionization dominates electron removal at high impact energies.

### 2.4 Classical over-barrier model

The classical over-barrier model (CBM) is applicable to multiply charged ion - atom collisions in the low keV impact energy range. It has been used extensively to calculate cross sections for (multi-) electron capture processes and to identify the main capture channels. We will mainly follow the CBM version proposed by Niehaus [40]. The model describes collisions of the type

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

i.e. a collision between a $q$-fold charged ion and target atom, in which $r$ electrons are transferred from the target to the projectile. Ionization processes are not considered here. CBM is based on the idea that electrons can transit from the target to the projectile at internuclear distances at which the height of the potential barrier between the target and the projectile is lower than the binding energy of the electrons.

Due to the Coulomb field of the ion the energy levels of the target electrons Stark shift and they become stronger bound:

$$E_i(R) = E_{b,i} - \frac{q}{R},$$

(2.32)
where $R$ is the internuclear distance and $E_{b,i}$ the binding energy of the $i$’th target electron. The potential experienced by the $i$’th electron is the potential of the approaching ion added to that of its own nucleus:

$$V^\text{in}_i(r) = -\frac{q}{|R - r|} - \frac{i}{|r|},$$

for $0 < |r| < |R|$, where $r$ is the coordinate of the $i$’th electron with respect to the parent nucleus. The height of the potential barrier between the ion and the atom depends on the internuclear distance. At the distance at which this height is equal to the Stark shifted binding energy the electron can escape the target potential. For the $i$’th electron this distance, the capture radius, is given by:

$$R^\text{in}_i = \frac{i + 2\sqrt{iq}}{-E_{b,i}}.$$  

At this distance the $i$’th electron is no longer localized on the target and moves in the joint potential well of the target and the projectile. CBM assumes that further on the way-in the shifted binding energy remains fixed, i.e. $E_j(R) = E_i(R^\text{in}_i)$ for $R \leq R^\text{in}_i$.

On the way-in electrons become sequentially quasi-molecular until the distance of closest approach is reached. After this point the potential barrier increases again. When the potential barrier between the projectile and the target equals the binding energies of the quasi-molecular electrons the quasi-molecular electrons have to ‘choose’ between being captured by the ion or recaptured by the target. The (re)capture processes are assumed to occur sequentially. Each capture or recapture process has an influence on the charges seen by the next electron to be captured or recaptured. This process is repeated until the least bound electron loses its quasi-molecular character. The internuclear distances at which (re)capture occur are given by:

$$R^\text{out}_i = R^\text{in}_i \left( \frac{\sqrt{q - c_i + i + c_i}}{\sqrt{q + i}} \right)^2,$$

in which $c_i$ is the number of already captured electrons at the moment that the $i$’th electron is either captured or recaptured. In case the $i$’th electron is captured by the projectile its binding energy at infinite internuclear distance is given by:

$$E_{b,i}^\text{final} = E_{b,i} - \frac{q}{R^\text{in}_i} + \frac{i + c_i}{R^\text{out}_i} = E_{b,i} [1 + \delta(q,i,c_i)],$$

where the function $\delta(q,i,c_i)$ is defined as:

$$\delta(q,i,c_i) \equiv \frac{1}{i + 2\sqrt{iq}} \left( q - \left( \frac{\sqrt{q + i}}{1 + \sqrt{q / i + c_i}} \right)^2 \right).$$

Thus if an electron is transferred to the projectile, it is predicted to be captured in a more strongly bound state than initially at the target (because $\delta > 0$). An example of the different stages of the CBM description are shown in figure 2.6 for one-electron capture in $A^6^+ + \text{Na}(3s)$

---

2Here we switch from ionization potential $I$ to binding energy $E_b$, defined to be negative, i.e. $E_b = -I$. 

---
collisions. CBM can also be used to obtain the Q-value, defined as the difference in electronic energy after and before the collision, by realizing that:

\[
Q_{\text{CBM}} = \sum_i (E_{b,i}^{\text{final}} - E_{b,i}^{\text{b}}) = \sum_i E_{b,i}^{\text{b}} \delta(q,i,c_i).
\]  

The cross section for the capture of \( r \) electrons is linked to the geometrical cross section defined by \( R_r^{\text{in}} \) and \( R < R_r^{\text{in}} \):

\[
\sigma_r = f_r \pi \left[ (R_r^{\text{in}})^2 - (R_{r+1}^{\text{in}})^2 \right]
\]  

in which \( f_r \) is a probability factor between 0 and 1, related to the chance of capture or recapture. However, also processes in which more than \( r \) electrons are active (\( R < R_r^{\text{in}} \)) should be considered and a more general form of equation 2.39 can be found in [40]. Here we assume that these processes do no contribute significantly. It has been suggested that \( f \) is related
Figure 2.7: CBM projectile charge state dependencies of a) the Q-value, b) the capture radius of the outermost electron, c) the capture probability (equation 2.40) and d) the one-electron capture cross section. The quantities have been calculated for Na(3s) (—) and Na\textsuperscript{*}(3p) (– –).

To the respective density of states in the projectile and in the target. Then $f_r$ is given as $\prod_i W_i$, where the probability of capture $W_i$ of the $i$’th electron is given by, using a hydrogenic approximation:

$$W_i = \frac{n_f^2}{n_f^2 + n_i^2},$$

(2.40)

where $n_i$ and $n_f$ are the principal quantum numbers of the electronic states on the target and the projectile, respectively. The cross sections are independent of the impact energy, just as in the Bohr-Lindhard model at low energies.

In figure 2.7 some of the discussed quantities are plotted as a function of the projectile charge state for one-electron capture from Na(3s) and Na\textsuperscript{*}(3p). Several observations can be made. First of all, CBM predicts always negative Q-values, i.e. capture into stronger bound states, and they become more negative for increasing projectile charge state. The difference in Q-value between capture from Na(3s) and Na\textsuperscript{*}(3p) increases. The capture radius increases with increasing projectile charge and decreasing binding energy, which is directly reflected in the total cross section. Note that one-electron capture from Na occurs at large internuclear distances, $R_1^\text{in} > 15$ a.u., leading to cross sections well above $1 \times 10^{-14}$ cm\textsuperscript{2}.
2.4 Classical over-barrier model

Figure 2.8: CBM reaction windows for one-electron capture of the least bound electron in collisions of He\(^{2+}\) and O\(^{5+}\) projectile ions on Na(3s) and Na\(^{\dagger}\) (3p) target atoms, where the Q-values of the relevant capture channels are indicated.

So far it is assumed that an electron is resonantly transferred to a projectile state with a binding energy \(E_{\text{final}}^{\text{b,i}}\). However, due to the quantized nature of the electronic states, this assumption is in general not fulfilled. Therefore it is assumed that several states near \(E_{\text{final}}^{\text{b,i}}\) get populated [40]. The width of this so-called reaction window is determined by the Heisenberg uncertainty relation \(\Delta E \Delta t \simeq 1\).

The Heisenberg uncertainty principle introduces an uncertainty in the energy definition, because the transition is made in a limited time interval (similar to the Massey criterion in section 2.2). The change in the barrier height can be written as:

\[
\Delta V = \frac{dV}{dt} \Delta t = \frac{dV}{dR} v_{\text{rad}} \Delta t.
\]  

Assuming that the classical uncertainty \(\Delta V\) is equal to the minimum quantum-mechanical uncertainty \(\Delta E\), one obtains:

\[
\Delta V = \sqrt{\left| \frac{dV}{dR} \right| v_{\text{rad}}}. \tag{2.42}
\]
Of all transferred electrons the uncertainties or energy widths connected to the over-barrier transitions on the way-in and way-out are added quadratically, leading to a total energy width $\Delta Q$. The reaction window of a particular process is now defined by a Gaussian distribution around the predicted $Q^{\text{CBM}}$ with $\Delta Q$ the width of the distribution, i.e.,

$$W(Q) = \frac{1}{\sqrt{\pi} \Delta Q} \exp \left( - \left( \frac{Q - Q^{\text{CBM}}}{\Delta Q} \right)^2 \right).$$  \hspace{1cm} (2.43)

$\Delta Q$ is proportional to $\sqrt{v_p}$. Thus with increasing impact energy the reaction window broadens, allowing a larger range of accessible $Q$-values.

In figure 2.8 the reaction windows for one-electron capture (of the least bound electron) in collisions of $\text{He}^{2+}$ and $\text{O}^6+$ on $\text{Na}(3s)$ and $\text{Na}^*(3p)$ are shown. A detailed discussion of the comparison between the model and experimental data is given in chapter 9. Here we can already state that the assignment of the main capture channels is in agreement with the experiments and with more sophisticated theoretical calculations.

CBM also allows for estimates of scattering angles or transverse momenta. As the charge states of the two nuclei are known at each part of the projectile trajectory, one can calculate the Coulomb repulsion along the trajectory. The Coulomb force between two point charges $q_1$ and $q_2$ at a distance $R$ from each other is given by:

$$F = \frac{q_1 q_2}{R^2} \mathbf{e}_R.$$

To calculate the integral force between the projectile and target straight-line trajectories of the projectile characterized by the projectile velocity $v_p$ and impact parameter $b$ are used (see figure 2.9). The component of the force perpendicular to the projectile ion’s trajectory is then given by (taking the origin at the target):

$$F_y = \frac{q_1 q_2 b}{(x^2 + b^2)^{3/2}},$$  \hspace{1cm} (2.45)

which has to be integrated over time to obtain the transverse momentum:

$$p_{\text{trans}} = \int F_y \, dt = \frac{1}{v_p} \int F_y \, dx.$$  \hspace{1cm} (2.46)

where the target is assumed to be fixed during the interaction, which is justified because the momentum transfer is small enough such that during the time of the interaction the target does not change its position significantly.

From CBM the values of $q_1$ and $q_2$ along the projectile trajectory are deduced. As an example, the situation for two-electron capture is depicted in figure 2.9. Only for distances smaller than $R_{1}^{\text{in}}$, at which a target electron starts to move in a quasi-molecular orbital, the particles start to repel each other. For every next electron the repulsion increases. On the way-out, the projectile charge is reduced by capturing electrons. If after the last electron transfer the projectile is still charged, i.e. after $\bar{R}$ passed $R_{1}^{\text{out}}$, a Coulomb force between the projectile and the target remains present, giving rise to a so-called ‘post-collision interaction’ (PCI). However, $R_{1}^{\text{out}}$ is usually so large that the effect of PCI on the transverse momentum
is small. Most of the transverse momentum is obtained near the distance of closest approach, i.e., when $R \simeq b$.

Applying equation 2.46 to every distinct segment of the trajectory and adding the results, leads to the following expression:

$$p_{\text{trans}}(b) = \frac{1}{v_p b} \left( \sum_i \left[ q \sqrt{1 - (b/R_i^{\text{in}})^2} + t_i \sqrt{1 - (b/R_i^{\text{out}})^2} + (q - r) r \right] \right),$$  

(2.47)

where $t_i = (q - c_i)(i + c_i) - (q - c_{i-1})(i - 1 + c_{i-1})$, and $r$ is the total number of captured electrons. The summation is over the number of active electrons. The transverse momentum is inversely proportional to the projectile velocity, and in first order to the impact parameter, too. The last term is associated with PCI. For one-electron capture of the least bound target electron, $t_1 = 1$ and $R_1^{\text{in}} = R_1^{\text{out}} \equiv R_1$, equation 2.47 reduces to:

$$p_{\text{trans}}(b) = \frac{1}{v_p b} \left[ (q + 1) \sqrt{1 - (b/R_1)^2} + (q - 1) \right].$$  

(2.48)

To obtain the transverse momentum distribution one has to consider the differential cross section in transverse momentum:

$$\frac{d\sigma}{dp_{\text{trans}}} = \frac{d\sigma}{db} \left| \frac{db}{dp_{\text{trans}}} \right| = 2\pi b \left| \frac{db}{dp_{\text{trans}}} \right|,$$  

(2.49)

where the relation $\sigma = \pi b^2$ is used. From equation 2.47 the derivative $dp_{\text{trans}}/db$ can be calculated. Thus, in order to obtain the transverse momentum distribution one calculates for the relevant impact parameters $b$ the transverse momentum $p_{\text{trans}}$ via equation 2.47 and its strength via equation 2.49.

The differential cross section, i.e., the projectile scattering angle dependent cross section, can be obtained via the relation $p_{\text{trans}} = m_p v_p \theta$, where $\theta$ is the projectile scattering angle and $m_p$ is the projectile mass. In figure 2.10 transverse momentum and scattering angle distributions are plotted for one-electron capture in He$^{2+}$ and O$^{6+}$ collisions on Na(3s) at $v_p = 0.5$ a.u.. Two effects have to be taken into account in comparing the dependence of the
transverse momentum on the projectile charge state. Of course with higher charge state the repulsion is increased, however, also the distances at which charge transfer can take place increase, thereby reducing the repulsion. From figure 2.10 it is seen clearly that the first effect dominates, leading to higher transverse momenta for higher projectile charge states. For the scattering angle distribution an apparent opposite effect is observed. This is due to the different projectile masses (note that $p_{\text{trans}}$ is independent of $m_p$). The heavier the projectile, the smaller its deflection for a given transverse momentum.

2.5 Close-coupling methods

The close-coupling or coupled channel method is a standard theoretical approach to treat charge transfer and excitation processes in a fully non-perturbative quantum-mechanical framework. It has extensively been described in the literature and general reviews can be found in [18, 19, 55]. The key assumption of the close-coupling description is that the electrons move between only a restricted number of configurations during the atomic collision.

The electronic wavefunction $\Psi(\mathbf{r}, t)$ is expanded on a finite basis set of states $\psi_k(\mathbf{r}, t)$ according to,

$$
\Psi(\mathbf{r}, t) = \sum_{k=1}^{M} a_k(t) \psi_k(\mathbf{r}, t),
$$

(2.50)

with the initial condition $a_i(-\infty) = 1$, i.e. $\Psi(\mathbf{r}, -\infty) = \psi_i(\mathbf{r}, t)$. The time-dependent Schrödinger equation,

$$
i\frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = H(t) \Psi(\mathbf{r}, t),
$$

(2.51)

is solved for the basis expansion of the wave function, resulting in a set of $M$ coupled equa-
tions:

\[
i \sum_{k=1}^{M} \langle \psi_j | \psi_k \rangle \frac{da_k(t)}{dt} = \sum_{k=1}^{M} a_k(t) \langle \psi_j | H(t) - i \frac{\partial}{\partial t} | \psi_k \rangle, \quad j = 1, \ldots, M, \tag{2.52}
\]

which for an orthonormal basis set results in:

\[
i \frac{da_j(t)}{dt} = \sum_{k=1}^{M} a_k(t) \langle \psi_j | H(t) - i \frac{\partial}{\partial t} | \psi_k \rangle, \quad j = 1, \ldots, M. \tag{2.53}
\]

The right-hand side of equations 2.52 and 2.53 describes the couplings between the different states which induce the transitions.

In general, the Hamiltonian for a \(N\)-electron system can be written as,

\[
H(t) = T + V(t) = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^{N} \left( -\frac{Z_T}{r_i} - \frac{Z_P}{|r_i - R(t)|} \right) + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}, \tag{2.54}
\]

which contains the kinetic energy of the electrons, the attractive Coulomb interaction with the target nucleus and projectile, and the Coulomb interaction between the electrons themselves. \(Z_P\) and \(Z_T\) are the charge states of the projectile and target nucleus, respectively, \(r_i\) is the position of the \(i\)th electron with respect to the target center and \(R(t)\) is the internuclear distance between the projectile and the target. The latter introduces a time dependence. Most often straight-line classical trajectories are used.

Traditionally the basis set expansion consists of molecular orbitals (MO) or atomic orbitals (AO), but also other types can be applied, for example Sturmian pseudo-states or analytical spline functions. For not too slow collisions one usually has to include so-called electron translation factors, taking into account the motion of the projectile with respect to the electron in the target frame. These factors restore the Galilean invariance of the system of coupled equations.

There exist one-center expansions which are restricted to orbitals centered around the projectile or target, two-center expansions with both projectile and target centered orbitals, or even three-center expansion, which usually also include orbitals centered at some point between the projectile and target (to take ionization explicitly into account). For the hypothetical case of complete basis sets two- or three-center expansions are in principle redundant and a one-center expansion is sufficient. However, due to the fact that in practice one is always limited to finite basis sets, such two- and three-center expansions are necessary to reach convergence for a reasonable number of basis functions and moreover to facilitate the projection of the final wavefunction onto the final states of interest.

The probability to find the system in final state \(f\) after the collision is given by,

\[
P_f(b) = |a_f(\infty)|^2, \tag{2.55}
\]

in which \(a_f\) is the (complex) transition amplitude. The coupled equations have to be solved for a range of impact parameters. The cross sections are obtained by integrating the probabilities over the impact parameter range (equation 2.16).

It is possible to calculate angular-differential cross sections within the straight-line trajectory approximation by means of a Bessel transformation of the transition amplitudes \(a_f\).
This may sound contradictory but it has been shown from quantum scattering theory that the differential cross section (DCS) is given by [56]:

$$\sigma_f(\theta) = \mu^2 v_p^2 \left| \int_0^{\infty} b a_f J_{|\Delta m|} (\mu v_p b \theta) \, db \right|^2$$

(2.56)

in which $\Delta m$ is the difference in $m$-quantum numbers of the initial state and final state $f$, $J_{|\Delta m|}$ is the Bessel function of order $\Delta m$, and $\mu$ is the reduced mass. The derivation of equation 2.56 lies outside the straight-line approximation. However, the crucial point is that the transition amplitudes $a_f$ can be taken from the straight-line approximation. The calculation of the DCS’s requires the computation of transition amplitudes $a_f$ for many more impact parameters $b$ than required for total cross sections, and is therefore a very demanding task (see e.g. [57, 58]).

In close-coupling calculations it is of key importance to include as many as possible states in the basis set. For charge transfer usually many final states are populated and therefore a very large basis set is needed. Especially for collision velocities close to the orbital velocity of the active electron, charge transfer populates a broad distribution of final states. Note that calculating the probability for capture into a certain final state with principal quantum number $n$, requires the computation of all $|m|$ substates within all possible $l$-states. The basis set size is generally limited by computational power.

Close-coupling methods have mainly been applied to one-electron transitions, i.e., one-electron capture, excitation or ionization. Although applied extensively, calculations on keV ion-alkali collision systems are basically limited to low charge state projectiles, i.e. $\text{H}^+$, $\text{He}^{2+}$ and $\text{Li}^+$. Studies with higher charge state projectiles are rather scarce [59]. Especially the combination of multiply charged ions and alkali-target atoms is a demanding task, because charge transfer takes place into high $n$-states of the projectile. However, with present-day computational power it becomes more and more feasible to handle the large basis sets necessary to describe transfer into high $n$-shells.

### 2.5.1 Basis generator method

Based on the concepts of time-dependent density functional theory the basis generator method (BGM), developed by Lüdde and Kirchner, is a close-coupling scheme designed to treat charge transfer and ionization processes in many-electron systems [60, 61]. The difference to other close-coupling methods rests on the idea how convergence can be achieved without resorting to very large basis sets: if the finite model space spanned by the basis functions is dynamically adapted to the problem at hand, couplings to that part of Hilbert space which is not covered are minimized. BGM has already proven its capabilities in a number of studies on ion collisions with atoms, ions, and molecules [62–64]. It has also been applied to laser-assisted ion-atom collisions [65, 66].

A (nonrelativistic) collision problem within the semiclassical approximation and the independent particle model involves the solution of time-dependent single-particle equations for all active electrons

$$i \frac{\partial \psi_i(r, t)}{\partial t} = H(t) \psi_i(r, t) \quad i = 1, \ldots, N.$$  (2.57)
where the subscript $i$ labels the electrons. A single-particle Hamiltonian is used that contains the kinetic energy, the Coulomb interaction with target and projectile nuclei, and a mean-field potential that accounts for the electron-electron interaction:

$$H(t) = -\frac{1}{2} \nabla^2 - \frac{Z_T}{|r_T|} - \frac{Z_P}{|r_P|} + v_{ee}(r,t). \quad (2.58)$$

In equations 2.57 and 2.58 $r$, $r_T$, and $r_P$ denote position vectors with respect to the center of mass, the target, and the projectile frames, respectively, and $Z_T$ and $Z_P$ are the nuclear charges. The mean-field potential $v_{ee}$ is discussed further below.

Essentially, the BGM is a coupled-channel method, i.e. the single-particle equations (2.57) are projected onto a finite set of basis states. Model spaces constructed by repeated application of a (regularized) Coulombic projectile potential onto atomic target eigenfunctions provide an appropriate dynamical representation of $\psi_i(r,t)$ [61]. Although this one-center version of BGM has been applied successfully to several one- and many-electron problems, its applicability to electron transfer processes is somewhat limited by the fact that bound projectile states are not included in the basis explicitly.

Therefore the BGM has been extended to a two-center version to investigate electron capture processes. The basis is generated from a finite set of $V_T$ target and $V - V_T$ projectile states taking into account Galilean invariance by the appropriate choice of electron translation factors:

$$\phi^0_v(r) = \begin{cases} \phi_v(r_T) \exp(i v t r) & \text{if } v \leq V_T \\ \phi_v(r_P) \exp(i v_p r) & \text{else} \end{cases} \quad (2.59)$$

where $v_T$ and $v_P$ are the corresponding constant velocities of the atomic frames. The $\phi^0_v$ states define a standard two-center atomic orbital expansion. They are augmented by BGM pseudo-states, which are constructed in the same way as in the one-center BGM method, namely by repeated application of a regularized projectile potential onto the target states,

$$\chi^\mu_v(r,t) = [W_p(t)]^\mu \phi^0_v(r) \quad \mu = 1, \ldots, M, \quad v = 1, \ldots, V_T \quad (2.60)$$

$$W_p(t) = \frac{1}{|r - R(t)|} \{1 - \exp[-|r - R(t)|]\}, \quad (2.61)$$

in which $R(t) = (b, 0, v_P t)$ denotes the classical trajectory of the projectile with impact parameter $b$. This set of pseudo states is eventually orthogonalized to the generating two-center atomic orbital basis (equation 2.59). The set of pseudo-states $\chi^\mu_v$ accounts for ionization channels and for quasimolecular effects at low collision velocity, which cannot be described by standard two-center atomic orbital expansions.

The single-particle wavefunction for the $k$-th active electron is represented in terms of the basis 2.60, i.e.

$$\psi_k(r,t) = \sum_{\mu=0}^{M(v)} \sum_{v=1}^{V} d^{i\mu v}_v(t) \chi^\mu_v(r,t), \quad M(v) = \begin{cases} M & \text{if } v \leq V_T \\ 0 & \text{else} \end{cases} \quad (2.62)$$

and the resulting set of ordinary differential equations for the coefficients $d^{i\mu v}_v(t)$ takes the form of equation 2.53. Bound-state probabilities for finding the $i$-th electron at the target ($p_i^{\text{tar}}$)
or at the projectile \((p_{i}^{\text{cap}})\) are calculated from the transition amplitudes within the generating basis (2.59), and single-particle probabilities for total ionization \((p_{i}^{\text{ion}})\) are obtained from the unitary requirement

\[
p_{i}^{\text{ion}} = 1 - p_{i}^{\text{tar}} - p_{i}^{\text{cap}}.
\]  

When integrated over the impact parameter total cross sections are obtained for capture and ionization of the \(i\)-th electron, that ignore the behavior of the other electrons.

Population probabilities of many-electron states are modelled by combining single-particle probabilities statistically. The most direct way to do this is the standard multinomial approach [67]. A deficiency of this model is the population of unphysical reaction channels, such as multiple capture into singly charged ions. To overcome this problem a modified combinatorial analysis, in which these unphysical channels are eliminated explicitly was suggested [68]. This so-called products-of-binomials model has been used with some success for collisions on oxygen and noble gas targets [68–71], but turned out to be unsuitable for Na targets. The model assumes that the product of a probability for capture of \(k\) electrons and an independent probability for ionization of \(l\) electrons equals the probability for simultaneous \(k\)-fold capture and \(l\)-fold ionization. While this is reasonable for a system with many near-identical electrons it leads to unphysical transfer ionization events in a system, whose dynamics is strongly dominated by a single valence electron. This becomes obvious in the limiting case that all inner-shell electrons are passive. Even in this one-active electron situation the product of one-electron capture and one-electron ionization probabilities is nonzero, implying the occurrence of transfer ionization. These difficulties cannot be remedied easily [72].

Finally, some remarks concerning the mean-field potential in the single-particle Hamiltonian of equation (2.58) are in order. For bare-ion impact on an atom it can be decomposed in a stationary atomic ground-state potential that accounts for the electron-electron interaction before the collision, and a contribution that models so-called response effects, i.e., time-dependent changes of the effective interaction due to changes of the electron density in the presence of the projectile

\[
v_{ee}(\mathbf{r}, t) = v_{ee}(t_{f}) + \delta v_{ee}(\mathbf{r}, t).
\]  

The role of response effects has been investigated for noble gas atoms [69, 70, 73–75]. It was found that they can be significant at impact energies in the low to medium keV regime. For Na those response models yielded only marginal differences with respect to the so-called no-response approximation, in which only the ground-state potential is taken into account. This is again a consequence of the fact that the electron dynamics in \(A^{q+}+\text{Na}\) collisions is strongly dominated by transitions of the single valence electron. Inner-shell and multielectron processes are possible but they are rather weak. The present study relies on the no-response approximation, i.e. the assumption \(\delta v_{ee}(\mathbf{r}, t) = 0\). The Na ground-state potential is obtained from the so-called exchange-only limit of the optimized-potential method of density-functional theory [76,77]. This means that static screening and exchange effects are fully included, but correlations are ignored.
2.6 Classical trajectory Monte Carlo

The classical trajectory Monte Carlo (CTMC) method relies on the classical calculation of the trajectories of all particles, i.e., projectile ion, target nucleus and electrons, taking into account the (screened) Coulomb interactions between them. Key ingredient is the sampling of the initial wavefunctions of the active target electrons, both in real and momentum space. The initial ensemble or ‘microcanonical distribution’ of target-centered electrons is constructed in such a way that it mimics the spatial and momentum properties of the initial state, i.e. $|\Psi_i(r)|^2$ and $|\Psi_i(p)|^2$. From the initial ensemble a member is randomly picked by the Monte Carlo technique. The Hamilton’s equations are solved numerically for a large number of trajectories which includes a random selection of relevant impact parameters.

Advantage of CTMC is that it yields both the ionization and electron capture cross sections consistently in the same calculations. CTMC has the equivalent of an infinite basis set which spans the ionization continuum too. The method is especially useful in the region of collision velocities comparable to the orbital electron velocities of the target atom where quantum theories are particularly difficult to apply. Furthermore, CTMC provides the complete momentum picture of the collision products. For each trajectory the momenta and impact parameter are saved, which makes the method quite suitable to act in conjunction with recoil-ion momentum spectroscopy.

First three dimensional three-body CTMC calculations of charge transfer and ionization were performed by Abrines and Percival for the $H^+ + H$ system [78]. The use of CTMC was extended to multiply charged ion collisions on hydrogen by Olson and Salop [79, 80] to investigate the dependence of the charge transfer and ionization cross sections on the projectile charge state. The $n,l$ distributions of one-electron capture in $A^q+ + H$ collisions were first extracted from the CTMC calculations by Salop [81] and Olson [82]. The electronic level of the ion after electron capture is determined by calculating the binding energy $E_b = -E$ of the electron from its kinetic energy in the projectile frame. A classical principal quantum number is assigned according to

$$n_c = \frac{q}{\sqrt{-2E_b}}. \tag{2.65}$$

The classical values are then “quantized” to a specific $n$ level via [83],

$$[n(n-0.5)(n-1)]^{1/3} \leq n_c \leq [n(n+0.5)(n+1)]^{1/3}. \tag{2.66}$$

The classical orbital angular momentum is defined by

$$l_c = [(x\dot{y} - y\dot{x})^2 + (x\dot{z} - z\dot{x})^2 + (y\dot{z} - z\dot{y})^2]^{1/2} \tag{2.67}$$

where $x, y, z$ are the Cartesian coordinates of the electron relative to the nucleus. Since $l_c^2$ is uniformly distributed for a given $n$ level, the quantal statistical weights are reproduced by choosing bin sizes such that [82]

$$l \leq (n/n_c) l_c \leq l + 1, \tag{2.68}$$

where $l$ is the orbital-angular-momentum quantum number. The $l_c$ values are renormalized by multiplying them by $n/n_c$ to reflect the fact that $l_c$ is linked to a non-integer $n_c$ value.
For three-body CTMC calculations involving multi-electron targets the interaction of the active electron with the core-electrons is represented by a model potential [84]. Such a representation seems ideally suited to quasi-one electron systems, such as the alkali-atoms. And indeed CTMC calculations have been quite successfully applied to one-electron capture and ionization in keV collisions on ground state and excited Na [85–92].

In order to address multi-electron capture and multiple-ionization processes Olson developed the so-called n-body classical trajectory Monte Carlo (nCTMC) method, in which all (active) electrons are explicitly incorporated. Besides the forces between the projectile ion and the target nucleus, those between the target nucleus and all its (active) electrons are included [93, 94]. Excluded are the electron-electron interactions, which are approximated by using effective charges for the parent nucleus to represent the average field experienced by each electron. For the Na-target 11-body CTMC calculations, which take into account the nine electrons of the Na L and M shells, have been performed for O\(^{6+}\)+Na(3s) [26] and He\(^{2+}\)+Na(3s) [95] collisions.