Theoretical Description of low energy collisions. Close-coupling semiclassical treatments

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1. Introduction

Collisions of ions with atoms and molecules at impact energies above 50 eV/a.m.u. are usually described by semiclassical methods. In these methods, the relative ion-atom (molecule) motion is treated by means of a classical trajectory and the remaining degrees of freedom are described quantally. There are two main reasons to introduce this approximation: Firstly, at these energies the full quantal treatment is very cumbersome because a large number of partial waves must be included. Secondly, it allows following the time evolution of the system, characteristic of classical descriptions, which helps to understand the collisional mechanisms. A complete explanation of the basis of the semiclassical approximation can be found in the text of Bransden and McDowell [1] and the references cited in it and will not be repeated here. The basic equations of this approach are outlined in section 2.

In this chapter we shall consider close-coupling (CC) methods to describe ion-atom and ion-molecule collisions. In the CC treatments the collisional wavefunction is expanded in terms of a complete set of functions. Therefore, the method is formally convergent, which in practice means that the accuracy of the results can be improved by adding more terms to the expansion, but the speed of convergence of a CC expansion depends on the basis set chosen and on the collision energy.

At low impact energies, charge transfer and excitation in ion-atom collisions are usually described by means of a CC expansion in terms of molecular functions, which is described for one-electron systems in section 3. When applying the CC molecular expansion it is required to include the so-called electron translation factors (ETF) (a review on this topic can be found in ref. [2]) and we summarize this point in section 4, using again a single-electron system to introduce it. For projectile velocities (v) larger than the target electron velocity (v_0), ionization starts to be sizeable, and this is the main limitation on the application of CC methods [3], which is also discussed in section

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4. The application of CC methods at high v is particularly relevant because of the very detailed experiments, like those based on ion recoil momentum spectroscopy [4], carried out in this energy range.

In section 5 we consider the application of the molecular expansion to many-electron systems. The main difficulty of this extension is the accurate calculation of energies and non-adiabatic couplings, which requires the application of quantum chemistry techniques (see [5]). We also describe in this section the use of some quantum chemistry packages (MRCI) and effective potentials, which are fundamental tools for calculations in ion-molecule collisions (see e.g. [6], [7])

In section 6 we describe briefly the use of CC expansions in terms of atomic functions (see e.g.[8], [1]), which are commonly applied at higher energies ($v_0/2 \lesssim v \lesssim 2v_0$) than the molecular expansion. Several works have treated ionization in the framework of this atomic method by adding the so-called pseudostates to the basis (recent applications of this kind of formalism can be found in refs. [9, 10, 11, 12, 13]), and we shall describe several ways to define these pseudostates.

At even higher projectile velocities ($v > v_0$), non-CC methods, which will not be considered in this chapter, are often used. For example:

(i) Perturbative methods: the Born series and modified treatments like those based on the distorted wave approximation. An explanation of them can be found in ref. [14].

(ii) Statistical Monte Carlo treatments, where the motion of all particles is treated classically (see [15]).

An illustration of the application of different methods (molecular and atomic CC, classical Monte Carlo and distorted wave approximation) to multiply-charged ions collisions with H can be found in the recent work of ref. [16],

Ion-molecule collisions give rise to new physical processes like electron capture and excitation into particular vibrorotational states. Also charge transfer or excitation can lead to molecular dissociation by transitions to either vibrational or electronic continuum states. Multiple electron capture can also yield molecular dissociation; for example, double electron capture in collisions of multicharged ions with H_2 gives rise to the Coulomb explosion process, where two protons are formed. Although the basic theoretical methods to treat ion-molecule collisions, based on the CC method, are well established (see the reviews of refs. [17] [18]), the complexity of these systems, in particular the description of the molecular internal motion, has limited the number of calculations; as an example, only a few applications to ion-H_2 collisions were reported in ref. [19], published in 1998, and in practice, additional approximations are employed. In section 7, we consider, as a benchmark case, the CC treatment of ion-H_2 collisions, and we describe the application of the sudden approximation [20] for molecular rotation and vibration that we have employed in recent works (see e.g. [21]) to evaluate vibrationally resolved cross sections.

Atomic units are used throughout except where otherwise stated.

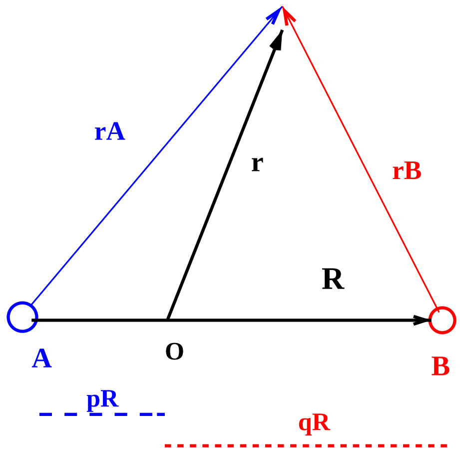

Figure 1.

2. The semiclassical approximation

We consider a collision system A + B, where B is a fully stripped ion and A is a single-electron ion or atom. In the semiclassical method, the nuclei follow a classical trajectory $\boldsymbol{R}(t)$, where $\boldsymbol{R}$ is the internuclear distance (see fig.1). In almost all applications the *eikonal* method is used, where the trajectory is rectilinear:

$$\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t \tag{1}$$

with $\boldsymbol{b}$, the impact parameter and $\boldsymbol{v}$ the relative velocity. The electronic motion is described by the wavefunction $\Psi(\boldsymbol{r}, t)$, which fulfills the equation (see e.g. [1]):

$$\left[H_{\rm el} - \mathrm{i} \left. \frac{\partial}{\partial t} \right|_{\mathbf{r}} \right] \Psi = 0 \tag{2}$$

where $\boldsymbol{r}$ is the position vector with respect to the origin O (see fig.1) and $H_{\rm el}$ is the clamped nuclei Hamiltonian in the Born-Oppenheimer approximation:

$$H_{\rm el} = -\frac{1}{2}\nabla_r^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R} \tag{3}$$

with $Z_{A,B}$ the nuclear charges, and $r_{A,B}$ the electron distances to the nuclei (see fig. 1). The symbol $\left.\frac{\partial}{\partial t}\right|_{\boldsymbol{r}}$ indicates that the derivative is carried out by keeping constant the electronic coordinates.

Equation (2) must be solved with the appropriate initial condition; this can be obtained by looking for the solutions of (2) in the limit when $t \to -\infty$. In particular, for a single-electron system, the semiclassical wavefunction $\Psi(\boldsymbol{r}, t)$ fulfills:

$$\begin{aligned}\Psi(\boldsymbol{r}, t) \underset{t \to -\infty}{\sim} & \ \Phi_i^A(\boldsymbol{r}_A) \exp\left[-\mathrm{i} \left(p\boldsymbol{v}\cdot\boldsymbol{r} + \frac{1}{2}p^2 v^2 t + E_i t + \alpha_A \right) \right] \\ = & \ \Phi_i^A(\boldsymbol{r}_A) D^A \exp\left[-\mathrm{i}(E_i t + \alpha_A) \right]\end{aligned} \tag{4}$$

which can be easily checked by substituting in (2) and taking into account the identity:

$$\left.\frac{\partial}{\partial t}\right|_{\boldsymbol{r}} = \left.\frac{\partial}{\partial t}\right|_{\boldsymbol{r}_A} + p\boldsymbol{v}\cdot\nabla_{\boldsymbol{r}} \tag{5}$$

where pR is the distance from the origin O to the nucleus A (see fig.1), and $\frac{\partial}{\partial t}\big|_{\boldsymbol{r}_A}$ indicates that the derivative is carried out by keeping constant the electronic coordinates referred to the nucleus A.

The function (4) includes:

(i) The atomic orbital (AO) $\Phi_i^A(\boldsymbol{r}_A)$, which describes the electronic orbital motion and is solution of

$$H^A(\boldsymbol{r}_A)\Phi_i^A(\boldsymbol{r}_A) = E_i\Phi_i^A(\boldsymbol{r}_A) \tag{6}$$

with

$$H^A(\boldsymbol{r}_A) = -\frac{1}{2}\nabla_r^2 - \frac{Z_A}{r_A} \tag{7}$$

(ii) The ETF [22] $D^A = \exp\left[-\mathrm{i}(p\boldsymbol{v}\cdot\boldsymbol{r} + p^2v^2t/2\right]$, which is a plane-wave that describes the translation of the electron attached to the nucleus A, with respect to the origin O.

(iii) The phase $\alpha_A = Z_B(Z_A - 1)v^{-1}\log(R - vt)$ that comes from the Coulomb interaction when the system is initially formed by two ions with charges Z_B and $Z_A - 1$.

Analogously, for elastic or excitation processes, the electron is attached to nucleus A in the limit $t \to \infty$, and a final state has the form

$$\begin{aligned}&\Phi_j^A(\boldsymbol{r}_A)\exp\left[-\mathrm{i}\left(p\boldsymbol{v}\cdot\boldsymbol{r} + \frac{1}{2}p^2v^2t + E_jt + \alpha_A\right)\right]\\ &= \Phi_j^A(\boldsymbol{r}_A)D^A\exp\left[-\mathrm{i}\left(E_jt + \alpha_A\right)\right]\end{aligned} \tag{8}$$

while for electron capture processes, one has:

$$\begin{aligned}&\Phi_k^B(\boldsymbol{r}_B)\exp\left[-\mathrm{i}\left(-q\boldsymbol{v}\cdot\boldsymbol{r} + \frac{1}{2}q^2v^2t + E_kt + \alpha_B\right)\right]\\ &= \Phi_k^B(\boldsymbol{r}_B)D^B\exp\left[-\mathrm{i}\left(E_kt + \alpha_B\right)\right]\end{aligned} \tag{9}$$

where qR is the distance from the origin O to the nucleus B. The ETF D^B describes the translational motion of the electron joined to nucleus B. Φ_k^B is solution of:

$$H^B(\boldsymbol{r}_A)\Phi_k^B(\boldsymbol{r}_A) = E_k\Phi_k^B(\boldsymbol{r}_B) \tag{10}$$

with

$$H^B(\boldsymbol{r}_B) = -\frac{1}{2}\nabla_r^2 - \frac{Z_B}{r_B} \tag{11}$$

and $\alpha_B = Z_A(Z_B - 1)v^{-1}\log(R - vt)$.

If $\Psi(\boldsymbol{r}, t)$ is solution of (2) with the initial condition (4), the probabilities for transitions to specific excitation and capture states are given respectively by:

$$P_{ij}^{\mathrm{exc}}(b, v) = \lim_{t\to\infty}\left|\langle\Phi_j^A D^A|\Psi\rangle - \delta_{ij}\right|^2 \;;\;\; P_{ik}^{\mathrm{cap}}(b, v) = \lim_{t\to\infty}\left|\langle\Phi_k^B D^B|\Psi\rangle\right|^2 \tag{12}$$

and the corresponding total cross sections can be obtained by applying the semiclassical approximation on the quantal boundary conditions leading to (see e.g. [1]):

$$\sigma_{if}(v) = 2\pi\int bP_{if}(b)\mathrm{d}b \tag{13}$$

3. The molecular expansion.

3.1. Basic equations.

At low collision energies, the interaction of the electron of the initial AO with the incoming ion takes place slowly, and this AO delocalizes forming a wavefunction of the (quasi)molecule. According to this physical picture, a CC expansion in terms of molecular orbitals (MOs) is employed for $\Psi(\mathbf{r},t)$:

$$\Psi^{MO}(\mathbf{r},t)=\sum_j a_j(t)\psi_j(\mathbf{r};R)\exp\left(-\mathrm{i}\int_0^t \varepsilon_j \mathrm{d}t'\right) \tag{14}$$

where the MOs, $\psi_j(\mathbf{r};R)$, are eigenfunctions of the clamped nuclei electronic Hamiltonian H_{el} of eq. (3):

$$H_{\mathrm{el}}\psi_j(\mathbf{r};R)=\varepsilon_j(R)\psi_j(\mathbf{r};R) \tag{15}$$

Substitution of eq. (14) in (2) leads to the system of differential equations:

$$\mathrm{i}\dot{a}_k=\sum_{j\neq k}\left\langle \psi_k\left|-\mathrm{i}\frac{\partial}{\partial t}\right|\psi_j\right\rangle a_j\exp\left[-\mathrm{i}\int_0^t(\varepsilon_j-\varepsilon_k)\mathrm{d}t'\right] \tag{16}$$

with $\dot{a}_k=\mathrm{d}a_k/\mathrm{d}t$. Initially, the system is described by the AO Φ_i^A, which corresponds to the asymptotic form of the MO ψ_i At very low velocities, the system behaves *adiabatically* and it can be described by the MO, ψ_i. As v increases, *non-adiabatic* transitions take place between the MOs, i.e., the coefficients a_k with $k\neq i$ are not zero and Ψ^{MO} becomes a superposition of several MOs, with $|a_k(t)|^2$ the population of a given MO. Since the MOs ψ_k can dissociate into excited AO of the target or with the electron attached to the projectile, excitation and charge transfer reactions take place through transitions between the MOs. From eq. (16), the importance of these transitions is determined by:

(i) The values of the integrals $\langle\psi_k\left|\frac{\partial}{\partial t}\right|\psi_j\rangle$, which are called *dynamical* or *non-adiabatic couplings.*

(ii) The energy differences $\varepsilon_j-\varepsilon_k$: When these differences are large, the phase factors $\exp\left[-\mathrm{i}\int_0^t(\varepsilon_j-\varepsilon_k)\mathrm{d}t'\right]$ oscillate quickly, and the effect of the dynamical couplings is canceled out when the system (16) is integrated along the trajectory.

Since $t=Z/v$, with Z the nuclear coordinate ($Z=\widehat{Z}\cdot\boldsymbol{R}$), when v increases, the dynamical couplings increase and the phases $\int_0^t(\varepsilon_j-\varepsilon_k)\mathrm{d}t'$ decrease. Consequently, non-adiabatic transitions are more significant at high v. In practice, this requires to enlarge the CC expansion (14) as v increases.

While eqs. (2),(4), (8) and (9) are expressed in a laboratory reference frame XYZ, with the Z axis in the direction of $\widehat{\boldsymbol{v}}$ and the X axis along the direction of $\widehat{\boldsymbol{b}}$, the MOs are calculated in a molecule-fixed rotating frame $X'Y'Z'$, with the Z' axis along the internuclear axis direction $\widehat{\boldsymbol{R}}$ (see fig. 2). When the dynamical couplings are expressed in the same frame, one obtains:

$$\left\langle\psi_k\left|\frac{\partial}{\partial t}\right|\psi_j\right\rangle=\frac{v^2t}{R}\left\langle\psi_k\left|\frac{\partial}{\partial R}\right|\psi_j\right\rangle-\frac{bv}{R^2}\left\langle\psi_k\left|\mathrm{i}L_{y'}\right|\psi_j\right\rangle \tag{17}$$

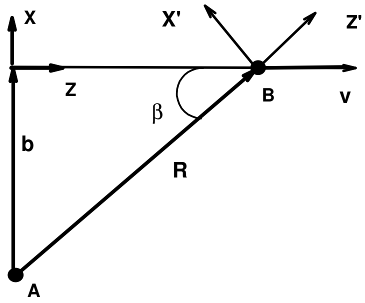

Figure 2.

where $L_{y'}$ is the Y' component of the electronic angular momentum:

$$\mathrm{i}L_{y'} = z'\frac{\partial}{\partial x'} - x'\frac{\partial}{\partial z'} \tag{18}$$

The dynamical couplings in (17) have two components:

(i) *Radial couplings*: $\left\langle \psi_k \left| \frac{\partial}{\partial R} \right| \psi_j \right\rangle$, which are due to the change of the MOs with the internuclear distance.

(ii) *Rotational couplings*: $\langle \psi_k | \mathrm{i}L_{y'} | \psi_j \rangle$, which are due to the rotation of the internuclear axis during the collision.

The first step in the application of the molecular expansion is the solution of eq. (15) to obtain the MOs and their energies. For one-electron systems, efficient techniques has been developed [23] to solve (15) and also to evaluate the dynamical couplings ([24]). Electronic energies and couplings are then substituted in the system (16), which is solved to obtain the coefficients $a_k(t)$ of eq. (14).

3.2. Mechanism of non-adiabatic transitions.

Some physical effects that give rise to non-adiabatic transitions are:

- **Avoided crossings.** In the avoided crossing between two potential energy curves, ε_j and ε_{j+1} approach, with a minimum of the energy difference $\varepsilon_{j+1} - \varepsilon_j$ at $R = R_0$. Then, the transition between the corresponding MOs, ψ_j and ψ_{j+1} becomes sizeable near R_0. Moreover, these MOs interchange their "characters" in the avoided crossing. Calling δ the width of the avoided crossing region, we have $\psi_j(R_0 + \delta/2) \simeq \pm\psi_{j+1}(R_0 - \delta/2)$, which gives rise to a radial coupling. In fact, for small δ, we can approximate the radial coupling between these MOs in the form:

$$\left\langle \psi_j \mid \frac{\partial \psi_{j+1}}{\partial R} \right\rangle \simeq \pm\frac{1}{\delta}\left\langle \psi_j(R_0 + \delta/2) | \psi_{j+1}(R_0 - \delta/2) \right\rangle \simeq \pm\frac{1}{\delta}, \tag{19}$$

  Radial couplings exhibit Lorentzian peaks in the neighborhood of avoided crossings, and transitions there are often described by means of the linear or Landau-Zener model [25].

- **Rotational transitions.** As an example of rotational transitions, we consider two MOs verifying:

$$\psi_j \underset{R\to 0}{\sim} p_{z'}\,;\quad \psi_{j+1} \underset{R\to 0}{\sim} p_{x'} \tag{20}$$

where $p_{x'}$, $p_{z'}$ are orbitals of the united atom, defined in the molecule fixed frame, which fufil

$$< p_{z'}|\mathrm{i}L_{y'}|p_{x'} >= 1$$

A rotation of a small angle θ about the axis Y' is carried out by the rotation operator

$$\exp(-\mathrm{i}\theta L_{y'}) \simeq 1 - \mathrm{i}\theta L_{y'}, \tag{21}$$

which yields in the limit $R \to 0$:

$$< p_{z'}|\mathrm{i}L_{y'}|p_{x'} >\simeq -(\theta)^{-1} < p_{z'}|\exp(-\mathrm{i}\theta L_{y'})|p_{x'} > \tag{22}$$

Physically, the effect of the quick rotation of the internuclear axis near $R = b$ is to leave the electron in an orbital which is a superposition of the two orbitals $p_{x'}$, $p_{z'}$, defined in the rotating frame.

- **Delocalization** We consider two orbitals with asymptotic behaviours:

$$\psi_j \underset{R\to\infty}{\sim} \Phi_j^A(\boldsymbol{r}_A);\quad \psi_{j+1} \underset{R\to\infty}{\sim} \Phi_{j+1}^B(\boldsymbol{r}_B) \tag{23}$$

As R decreases the MOs delocalize and can be represented by combinations of the form:

$$\psi_j = N_j\left(\Phi_j^A + \alpha(R)\Phi_{j+1}^B\right)\,;\ \psi_{j+1} = N_{j+1}\left(\Phi_{j+1}^B + \beta(R)\Phi_j^A\right) \tag{24}$$

At large internuclear distances, $< \Phi_j^B|\Phi_{j+1}^A >\simeq 0$, $< \Phi_j^A|\Phi_{j+1}^B >\simeq 0$, and then:

$$\left\langle \psi_j \mid \frac{\partial\psi_{j+1}}{\partial R}\right\rangle \simeq N_j N_{j+1}\frac{\mathrm{d}\beta}{\mathrm{d}R} \tag{25}$$

The mechanism of a given collision involves several radial and rotational transitions, whose relative importance is determined by the electronic energies and couplings of the particular system considered. An useful illustration of this mechanism is the "collision history"; i.e. the plot of the populations of the MOs, $|a_j(t)|^2$ as functions of t, which indicates how transitions occur during the collision.

In practice, one has to study the electronic energies and dynamical couplings to decide which MOs must be included in the CC expansion; this selection procedure involves in many cases a trial-and-error process, where more MOs are added to the initial expansion after checking that substantial transitions take place to them. Given that energies and dynamical couplings are different for each system, an independent calculation is required for each collision, which is not generally the case in the high v methods where calculation for series of systems are carried out by changing the input parameters.

3.3. Diabatic bases.

In some cases, radial couplings are very large (for example in narrow avoided crossings), which can cause numerical difficulties when solving (16). Then, it can be useful to employ a *diabatic* basis $\{\psi_j^d\}$, formed by linear combinations of the MOs $\{\psi_j\}$ (the adiabatic states), and therefore, the diabatic states are no longer eigefunctions of H_{el}. The CC expansion has then the form:

$$\Psi^d(\mathbf{r},t) = \sum_j a_j^d(t)\psi_j^d(\mathbf{r};R)\exp\left(-\mathrm{i}\int_0^t H_{jj}^d \mathrm{d}t'\right) \tag{26}$$

where

$$H_{jj}^d = \langle\psi_j^d|H_{\mathrm{el}}|\psi_j^d\rangle\,, \tag{27}$$

and the system of differential (16) must be replaced by:

$$\mathrm{i}\dot{a}_k^d = \sum_j \left\langle \psi_k^d \middle| H_{\mathrm{el}} - \mathrm{i}\frac{\partial}{\partial t} \middle| \psi_j^d \right\rangle a_j^d \exp\left[-\mathrm{i}\int_0^t (H_{jj}^d - H_{kk}^d)\mathrm{d}t'\right] \tag{28}$$

It must be noted that the electronic couplings $\langle\psi_k^d|H_{\mathrm{el}}|\psi_j^d\rangle$ are independent of v, while the dynamical couplings are proportional to v (see eq. (17)). So that, if the diabatic states are built up in such a way that the dynamical couplings are small, the transitions at high v between them will decrease with respect to those between the original adiabatic states.

In the particular case of a narrow avoided crossing of two energy curves, $\varepsilon_j, \varepsilon_{j+1}$, a diabatic basis $\{\psi_j^d, \psi_{j+1}^d\}$ can be defined by imposing that the peak of the radial coupling $\left\langle\Psi_j^d|\frac{\partial}{\partial R}|\psi_{j+1}^d\right\rangle$ vanishes, which leads to a crossing of the diabatic Hamiltonian diagonal matrix elements H_{jj}^d, H_{j+1j+1}^d. At high v, this crossing is traversed *diabatically*; i.e. the transitions between the diabatic states are small because the remaining electronic coupling is uneffective at high v. Hence, the diabatic basis is also useful to simplify the collision mechanism. Several definitions of diabatic states can be found in [5].

4. Translation factors. The CTF method.

The so-called *momentum transfer* or *electron translation problem* has been treated in many papers since it was pointed out in 1958 [22]. This difficulty is related to the presence of the ETFs in the initial condition (4). However, when the expansion (14) is employed, each basis function fulfils:

$$\psi_k(\boldsymbol{r};R) \underset{R\to\infty}{\sim} \Phi_k^{A,B}(\boldsymbol{r}_{A,B})\,, \tag{29}$$

which, unlike the correct initial and final conditions (eqs. (4), (8), (9)), does not contain any translation factor. At first sight, this does not seem to be a serious difficulty, because the molecular set is complete, and the linear combination (14) is able to describe any initial condition. However, in practice, truncated expansions are used that do not include continuum MOs, and then they cannot reproduce the ETFs which are continuum wavefunctions. It must be remarked that this is not only a formal problem, but neglecting the ETFs produces important practical difficulties such as non-vanishing asymptotic couplings and non-Galilean invariant cross sections.

The generally accepted solution to the ETF problem, is to modify the expansion (14) by multiplying each MO by a ETF to ensure that each basis function verifies asympotically the semiclassical equation. The most usual way to modify the molecular expansion is the common translation factor (CTF) method, proposed in ref. [26], and applied in many works (see [2]). In this method, all molecular functions are multiplied by *the same* ETF $D(\boldsymbol{r}, t)$, so that the CC expansion has the form:

$$\Psi^{\mathrm{CTF}}(\mathbf{r}, t) = D(\boldsymbol{r}, t) \sum_k a_k(t) \psi_k(\mathbf{r}; R) \exp\left(-\mathrm{i} \int_0^t \varepsilon_k \mathrm{d}t'\right) \tag{30}$$

Where the coefficients $a_k(t)$ are determined by substituting Ψ^{CTF} in the semiclassical equation (2), which leads to the system of differential equations:

$$\mathrm{i}\dot{a}_k = \sum_j \left\langle \psi_k D \left| H_{\mathrm{el}} - \varepsilon_j - \mathrm{i}\frac{\partial}{\partial t} \right| \psi_j D \right\rangle a_j \exp\left[-\mathrm{i} \int_0^t (\varepsilon_j - \varepsilon_k) \mathrm{d}t'\right] \tag{31}$$

The usual form of a CTF is:

$$D(\boldsymbol{r}, t) = \exp\left[\mathrm{i} U(\boldsymbol{r}, t)\right] \tag{32}$$

where the function U verifies:

$$\lim_{R \to \infty, r_A \text{ finite}} U = -p \boldsymbol{v} \cdot \boldsymbol{r} - p^2 v^2 t/2\,; \quad \lim_{R \to \infty, r_B \text{ finite}} U = q \boldsymbol{v} \cdot \boldsymbol{r} - q^2 v^2 t/2 \tag{33}$$

By comparing the definition of the CTF (eqs. (32) and (34)) with its asymptotic forms (33) , a simple interpretation of the CTF emerges: $\nabla U(\boldsymbol{r}, t)$ is an electronic velocity field, which is defined by means of a switching function, $f(\boldsymbol{r}, R)$:

$$U(\boldsymbol{r}, t) = f(\boldsymbol{r}, R) \boldsymbol{v} \cdot \boldsymbol{r} - f^2(\boldsymbol{r}, R) v^2 t/2 \tag{34}$$

where

$$\lim_{R \to \infty, r_A \text{ finite}} f(\boldsymbol{r}, R) = -p\,; \quad \lim_{R \to \infty, r_B \text{ finite}} f(\boldsymbol{r}, R) = q \tag{35}$$

Several switching functions have been used (see e.g., [26], [27], [28], [29]) and many other can be proposed. An example is [28]:

$$f(\boldsymbol{r}, R) = \frac{R}{R^2 + \beta^2} \boldsymbol{r} \cdot \widehat{\boldsymbol{R}} \tag{36}$$

where β is a parameter, which determines the extension of the region $R < \beta$ where U is small.

With the definitions of eqs. (34) and (35), each term of the CTF expansion (30) has the correct asymptotic behaviour, and the initial condition has the form:

$$\lim_{t \to -\infty} a_k(t) = \delta_{ik} \exp\left[-\mathrm{i} \int_0^t [E_i - \varepsilon_i(R)] \mathrm{d}t\right]\,, \tag{37}$$

while the transition probabilites are:

$$P_{if}(b, v) = \lim_{t \to \infty} |\langle \psi_f D | \Psi \rangle - \delta_{if}|^2 = \lim_{t \to \infty} |a_f(t) - \delta_{if}|^2 \tag{38}$$

The main advantges of the CTF method are:

(i) Since all MOs are multiplied by the same ETF, and since the MOs $\{\psi_k\}$ form a complete set, the set of modified functions $\{\psi_k D\}$ is also a complete, and therefore the method is formally convergent.

(ii) The modified dynamical couplings are calculated with a relatively modest computational effort when compared with not-common treatments.

(iii) The method is easily generalized to many-electron systems and diabatic bases.

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When a CTF is used, a kinematic effect is described: the nuclei drag the electron, but the CTF also introduces a dynamic effect: the dynamical couplings, and therefore the transitions between the MOs, are modified (see eq. (31)). However, the velocity field ∇U is irrotational [30] and cannot describe rotational transitions. Then, an appropriate CTF verifies $\nabla U = 0$ at small R, which permits that the rotational transitions be completely described by the unmodified rotational couplings. For example, the switching function of eq. (36) contains the cut-off factor $\frac{R}{R^2+\beta^2}$ in (36) yielding $\lim_{R\to 0} f = 0$, and accordingly $\lim_{R\to 0}(\nabla U) = 0$.

As mentioned above, the CTF expansion is formally convergent independently of the switching function employed, but different functions will lead to different convergence speeds. In fact, the choice of CTF is a problem similar to the choice of a basis set to evaluate atomic and molecular wavefuctions. This point of view has been used as a criterion, first suggested in ref. [31], to optimize CTFs; it requires that the choice of the CTF minimizes the couplings with the MOs not included in the basis. This idea is the basis of the so-called norm-method of ref. [32]. There is however a natural boundary of the method [33]: When v increases, ionization starts to be sizeable, and one finds that the CTF with the asymptotic behaviour of eq. (35) cannot describe the motion of the ionized electron and is no longer appropriate.

The behaviour of the CTF molecular method at high v has been studied in [2], [34] [35], [36] and [3], where several collisions of fully stripped ions with H were considered. There are two motivations for this study: First, the suggestion that the ionization process can be described by bound MOs, as a consequence of the "hidden crossing" mechanism (see [37]). Second, the results of several CC calculations that showed good agreement between calculated electron-loss (charge transfer + ionization) cross sections and the experimental ones, pointing out to a common molecular mechanism for charge transfer and ionization processes. We can summarize the main conclusions of these works as follows:

(i) the CTF method overestimates charge transfer total cross sections calculated for impact energies beyond their maxima.

(ii) Calculated charge transfer cross sections at high v show good agreement with experimental target electron-loss cross sections.

(iii) At short R, some modified functions $\chi_j D$ have positive energy with respect to both moving nuclei and then they can describe ionization, which explains the good agreement with experimental electron-loss cross sections. Nevertheless, this description is neccessarily incomplete, since the functions $\chi_j D$ are asympotically charge transfer or excitation channels, and the electronic flux that should yield ionization in the limit $t \to \infty$ overpopulates the charge transfer (and in some cases also the excitation) channels.

(iv) From the comparison with accurate ionizing wavefunctions [12], we have found that the CTF expansion attemps to represent the ionizing wavefunction by means of a very complicate combination of the modified functions $\chi_j D$, with a CTF that does not describe the motion of an ionized electron; this unphysical behaviour of the CTF does not allow to correctly represent the time evolution of the ionizing wavefunction, and the population remains "trapped" in some charge transfer states. The consequence of this trapping effect is that the wavefunction can be very different from the exact one and therefore, the expansion (30) is not useful to evaluate parameters such as momentum components of the ionized electron, which are more sensitive than total cross sections to the quality of the wavefunction.

(v) The apparent interlocking of charge transfer and ionization mechanisms at high v is mainly a consequence of the limitation of the CC expansion to describe ionization. The method attempts to represent the ionizing wavefunction by combining the states available, but this process is largely artificial.

5. Many-electron systems

In order to generalize the CC molecular expansion to many-electron systems, one must require that the collisional wavefunction be antisymmetric with respect to the interchange of the coordinates of two electrons. This requirement is easily fulfilled by the CTF wavefunction by taking:

$$U(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N, t) = \sum_{i=1}^{N} \left[f(\boldsymbol{r}_i, t)\boldsymbol{v} \cdot \boldsymbol{r}_i - f^2(\boldsymbol{r}_i, t)v^2 t/2 \right] \tag{39}$$

which is symmetric with respect to the electrons exchange, and with

$$\Psi^{\mathrm{CTF}}(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N, t) = \exp\left[\mathrm{i}U(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N, t)\right] \times \\ \times \sum_k a_k(t)\psi_k(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R) \exp\left(-\mathrm{i}\int_0^t \varepsilon_k \mathrm{d}t'\right) \tag{40}$$

where the many-electron molecular functions $\psi_k((\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R)$ are antisymmetric.

The main difference with the single-electron case is the difficulty of evaluating the many-electron molecular wavefunctions. In fact, because of the presence of the electron-electron repulsion potential, analytical molecular wavefunctions cannot be obtained, and the functions ψ_k of eq. (40) are approximate solutions of the Born-Oppenheimer electronic equation (15), which are evaluated by employing quantum chemistry techniques. A detailed explanation of these techniques can be found in quantum chemistry textbooks (see e.g. [38]) and their application in collisions has been considered in ref. [5]. In practice, the approximate molecular functions are expressed in terms of suitable basis functions, and the most usual are:

- Slater type orbitals (STO):
$$\xi^{STO}(\boldsymbol{r}; n, l, m, \alpha) = N_{\alpha,n,l} r^{n-1} Y_{lm}(\hat{\boldsymbol{r}}) \exp(-\alpha r) \quad (41)$$
where $N_{\alpha,n,l}$ is a normalization constant, n, l, m are integers, Y_{lm} is a spherical harmonic and α is a non-linear parameter.
- Gaussian type orbitals (GTO):
$$\xi^{GTO}(\boldsymbol{r}; n, l, m, \alpha) = N_{\alpha,n,l,m} x^n y^l z^m \exp(-\alpha r^2) \quad (42)$$
where $N_{\alpha,n,l,m}$ is a normalization constant, n, l and m are integers; x, y, z, the electron cartesian coordinates and α is a non-linear parameter.

5.1. Configuration interaction.

In the Configuration Interaction (CI) method, we look for an approximate solution of the electronic Schrödinger equation:

$$H_{\rm el}(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R)\psi_j(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R) = \varepsilon_j(R)\psi_j(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R) \quad (43)$$

where

$$H_{\rm el}(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N; R) = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{iA}} - \frac{Z_B}{r_{iB}} \right] + \sum_{i<j} \frac{1}{r_{ij}} + \frac{Z_A Z_B}{R} \qquad = H_{\rm core} + \sum_{i<j} \frac{1}{r_{ij}} \quad (44)$$

where ψ_j takes the form of a linear combination of N-electron wavefunctions ϕ_m called *configurations*:

$$\psi_j = \sum_m c_{mj}\phi_m \quad (45)$$

The configurations are built up from products of one-electron functions (*spin-orbitals*) $\chi_p(\boldsymbol{r}_i, \sigma_i)$. The spin-orbitals are products of orbitals $\varphi(\boldsymbol{r}_i)$ (e.g., STOs, GTOs, etc.), and spin wavefunctions α, β, with spin quantum number $m_s = +1/2$ and for $m_s = -1/2$ respectively. A configuration is a linear combination of a few products of spin-orbitals of the form:

$$\phi_m = \sum_\lambda d_{m\lambda} \prod_p \chi_p^\lambda(\boldsymbol{r}_p, \sigma_p) \quad (46)$$

where the constant coefficients $d_{m\lambda}$ are chosen so as the configuration ϕ_m verifies the following conditions:

- It is antisymmetric with respect to the interchage of two electrons.
- It is an eigenfuction of the spin operators S^2 (it has a given multiplicity) and S_z.
- It is symmetry adapted: it has the symmetry of an irreducible representation of the molecular point group. For example, for atomic calculations, a configuration must be an eigenfunction of the orbital angular momentum operators L^2 and L_z.

To illustrate these definitions, we consider the well-known example of He 1s2s configurations (see e.g. [38]) One considers two orbitals (1s and 2s) and then there are four spin-orbitals: 1sα, 1sβ, 2sα, 2sβ. The possible spin-orbital products are: 1sα(1) 2sα(2), 1sα(1) 2sβ(2), 2sα(1) 1sα(2), 2sα(1) 1sβ(2), 1sβ(1) 2sα(2), 1sβ(1) 2sβ(2), 2sβ(1) 1sα(2), 2sβ(1) 1sβ(2), and a ^{1}S configuration is:

$$\frac{1}{\sqrt{2}}\left[\,\|1\mathrm{s}\alpha(1)2\mathrm{s}\beta(2)\| - \|1\mathrm{s}\beta(1)2\mathrm{s}\alpha(2)\|\,\right]$$

where the symbol $\|\ \|$ indicates a (normalized) Slater determinant; this is equivalent to

$$\frac{1}{2}\left[(1\mathrm{s}(1)2\mathrm{s}(2) + 2\mathrm{s}(1)1\mathrm{s}(2))\,(\alpha(1)\beta(2) - \beta(1)\alpha(2))\right]$$

This function is obviously antisymmetric, the combination of spin wavefunctions is eigenfunction of S^2 with $S = 0$, and the spatial wavefunction is eigenfunction of L^2 with $L = 0$, then it is a ^1S configuration. Analogously, in the molecular case, configurations are built from products of spin-molecular-orbitals. For example, a configuration $^1\Sigma_g^+$ of H_2 is of the form:

$$\|\sigma_g\alpha(1)\sigma_g\beta(2)\| = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2)\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

where σ_g is a MO of this symmetry.

To determine the coefficients c_{jm} the variational method is applied (see e.g. [38]). In this method, one looks for the coefficients that minimize the energy expectation value:

$$\overline{\varepsilon_j} = \frac{\langle\psi_j|H_{\mathrm{el}}|\psi_j\rangle}{\langle\psi_j|\psi_j\rangle} \tag{47}$$

The minimum condition $\delta\overline{\varepsilon_j} = 0$ leads to the secular equation:

$$(\boldsymbol{H} - \overline{\varepsilon_j}\boldsymbol{S})\boldsymbol{c_j} = 0 \tag{48}$$

where $\boldsymbol{H}$, and $\boldsymbol{S}$ are respectively the Hamiltonian and overlap matrices, whose elements are:

$$\begin{aligned} H_{mn} &= \langle\phi_m|H_{\mathrm{el}}|\phi_n\rangle \\ S_{mn} &= \langle\phi_m|\phi_n\rangle\,, \end{aligned} \tag{49}$$

and the solution of eq. (48) is the column vector $\boldsymbol{c_j}$ whose elements are the coefficients c_{mj}.

The application of the molecular expansion with CI wavefunctions involves the calculation of the dynamical couplings $\langle\psi_j|\partial/\partial t|\psi_k\rangle$, which will be considered in section 5.5, and the solution of the system of differential equations (31). An important difficulty of the use of the variational method comes from the fact that the phase of the approximate solutions ψ_j of eq. (44) is arbitrary. In practice, since the configurations ϕ_m are usually real functions, this results in an arbitrary sign of the solutions of (48), (and consequently, arbitrary signs of the dynamical couplings) which in actual calculations changes randomly as a function of R. Therefore, the method involves a painstaking first step (also required for SCF and MRCI wavefunctions) of removing random signs before substituting the corresponding couplings in (31). The CI method has been applied in our laboratory to obtain molecular wavefunction for several two-electron collision systems; e.g. He^+-H [39] H^+-H^- [40], Li^{2+}-H [41].

An alternative to the CI method is to expand directly the collisional wavefunction in a basis set of configurations [42]. For a two-electron system, this expansion has the form:

$$\Psi_{\rm cf}^{\rm CTF}(\boldsymbol{r}_1,\boldsymbol{r}_2,t) = D(\boldsymbol{r}_1,\boldsymbol{r}_2,t)\sum_k a_k(t)\phi_k(\boldsymbol{r}_1,\boldsymbol{r}_2;R)\exp\left(-{\rm i}\int_0^t H_{kk}{\rm d}t'\right) \quad (50)$$

where the configurations ϕ_k are products of MOs of a one-electron system, and then they are not eigenfunctions of $H_{\rm el}$. The advantage of this method is that the calculation of dynamical coupling is easier than between CI wavefunctions and the sign of the configurations do not change randomly. The disadvantage is that larger basis sets than for the CI expansion are required. Expansion (50) has been applied in refs. [29], [43] to study single and double capture in collisions of multiply charged ions (C^{6+}, N^{7+}, O^{8+}, Ne^{8+}, Ne^{10+}) with He, including double capture into autoionizing states.

5.2. The SCF method.

In the Self Consistent Field (SCF) method, a single configuration approach is employed, and the variational method is applied to determine the "best" orbitals, which define this configuration. The simplest case is a closed-shell configuration, in which all orbitals are doubly occupied and this configuration has the form:

$$\psi_j = \left\| \varphi_1\alpha(1)\varphi_1\beta(2)...\varphi_{N/2}\alpha(N-1)\varphi_{N/2}\beta(N) \right\| \,, \quad (51)$$

which is called the Restricted Hartree-Fock (RHF) method. In the variational method, one requires the condition: $\delta[\langle\psi_j|H_{\rm el}|\psi_j\rangle] = 0$ for small variations $\delta\varphi_p$ with the restrictions $\langle\varphi_p|\varphi_q\rangle = \delta_{pq}$.

Usually, the orbitals φ_p are expressed as linear combinations of a set of n ($n > N$) basis orbitals, $\{\xi_s\}$, (for example STOs or GTOs):

$$\varphi_p = \sum_{s=1}^{n} b_{sp}\xi_s \,, \quad (52)$$

and the application of the variational method yields a set of equations with the form of a secular equation for the coefficients b_{ps}, which define the so-called canonical orbitals: [44]:

$$(\boldsymbol{\mathcal{F}} - \boldsymbol{\mathcal{S}}\varepsilon_p)\,\boldsymbol{b}_p = 0 \,, \quad (53)$$

where $\boldsymbol{b}_p$ is a column vector with components b_{sp}, $\boldsymbol{\mathcal{S}}$ is the overlap matrix in the $\{\xi_s\}$ basis and $\boldsymbol{\mathcal{F}}$ is the matrix of the Fock operator:

$$\begin{aligned}\mathcal{F}_{st} &= \langle\xi_s|H_{\rm core}|\xi_t\rangle + \\ &+ \sum_{p=1}^{N/2}\sum_{q,r}^{n} b_{qp}b_{rp}\left[2\left\langle \xi_s\xi_q\left|\frac{1}{r_{12}}\right|\xi_t\xi_r\right\rangle - \left\langle \xi_s\xi_q\left|\frac{1}{r_{12}}\right|\xi_r\xi_t\right\rangle\right]\end{aligned} \quad (54)$$

The eigenvalue ε_p in (53) is interpreted as the energy of the electron decribed by the orbital φ_p in the average field created by the nuclei and the remainder $N-1$ electrons, which occupy the orbitals that define the configuration (51). Since the Fock matrix elements (54) depend on the coefficients b_{qp}, which are the solutions of (53), this latter equation must be solved iteratively.

For open-shell configurations, the unrestricted Hartree-Fock (UHF) method is usually employed, where a treatment similar to that of eqs. (52)- (54) is applied, but the restriction of the same orbital part for two spin-orbitals (with α and β spin functions) of eq. (51) is removed. Therefore, a configuration of the form:

$$\psi_j = \|\varphi_1\alpha(1)...\varphi_m\alpha(m)\varphi_{m+1}\beta(m+1)\varphi_N\beta(N)\| \ , \tag{55}$$

is used. Although, SCF methods have been widely employed in static problems, their usefulness in dynamics is limited by the fact that they are not appropriate to evaluate excited states wavefunctions, and are normally used as the starting point of a CI calculation.

5.3. MRCI methods.

These methods start from the SCF treatment, and although the same arguments apply to the UHF method, we take, as an example, the RHF-SCF case; this provides a set of n canonical orbitals $\{\varphi_s\}$, solutions of (53), with n the size of the basis set (see eq. (52)). These orbitals can be classified into two sets: 1)*Occupied* orbitals: the $N/2$ orbitals of lowest energy, which are those defining the ground state configuration (51). 2) *Virtual* or unoccupied orbitals: The remainder $n-N/2$ orbitals.

In order to obtain wavefunctions for excited states, the SCF orbitals can be used to construct a set of configurations by promoting electrons from the occupied orbitals to the virtual ones. As an example, the excitation of two electrons from the last occupied orbital $\varphi_{N/2}$ in eq. (51) to the first virtual $\varphi_{N/2+1}$ gives rise to the antisymmetrized product of spin-orbitals:

$$\psi_k = \left\|\varphi_1\alpha(1)\varphi_1\beta(2)...\varphi_{N/2+1}\alpha(N-1)\varphi_{N/2+1}\beta(N)\right\| \ , \tag{56}$$

This set of configurations is then employed as a basis for a CI calculation. As long as all excitations are permitted, the difference between occupied and virtual orbitals is irrevelant. However, the size of the resulting configurations set can be very large, and some simplifications are often introduced in many-electron calculations; for example, only single and double excitations are allowed. This approximation provides an accurate energy for the ground state, for which the occupied orbitals were optimized in the SCF step, but to less accurate results for the excited states. In dynamical calculations, the transitions are determined by the energy differences (see eq. (16) of section 2), and it is desirable to evaluate with similar accuracy all states included in the basis, and a better alternative to this treatment are the multirreference CI (MRCI) methods. The scheme of a MRCI calculation is as follows:

(i) SCF calculation to obtain a set of canonical orbitals $\{\varphi_p\}$.

(ii) Definition of a reference configurations set: This set is formed by a few configurations build up from products of the spin-orbitals obtained in the SCF step, and which usually includes the SCF configuration. These configurations are assumed to provide a reasonable description of the states required.
(iii) Construction of a CI space by allowing excitation (normally single and double excitations) from the reference configurations.
(iv) Solution of the secular equation (48) with $\boldsymbol{S} \equiv \mathbf{1}$.

In practice, a first MRCI calculation is carried out at infinite internuclear separation for the atomic states involved in the collision, to compare the calculated energies with the corresponding spectroscopic values. The reference configurations are chosen in order to achieve a given precision in the atomic energies. For finite R, where experimental data are not in general available, the reference set is changed with the criterion of keeping an approximate constant weight (the sum of the squares of the CI coefficients) (of about 95%) of the reference configurations in the final wavefunctions. The application of MRCI methods in atomic collision is carried out by employing the quantum chemistry packages in which this technique has been implemented. Some examples of the application of MRCI packages to collisions involving doubly charged ion are the following:

- Ne^{2+} + H collisions have been studied [45] by using the package GAMESS [46].
- C^{2+} + H collisions have been studied in refs. [47] and [48], by using the packages MRDCI [49] and MELD [50], respectively
- O^{2+} + H collisions have been considered in ref. [51] . The MRCI calculation employed a CI method based on the the package CIPSI [52].
- C^{2+} +He collisions have been studied in [53] by using MELD.

5.4. Effective potentials.

In some collision processes there is a clear distinction between the *active* electron, which is exchanged or excited during the collision, and the remainder (*core*) electrons. As an example, in the collision C^{4+} + H, at low energies ($E <$ 10keV/a.m.u.), only the electron capture process:

$$C^{4+}(1s^2\ {}^1S) + H(1s) \rightarrow C^{3+}(1s^2 nl) + H^+ \tag{57}$$

is relevant. In this process, the active electron interacts with a core formed by the nuclei and the $1s^2$ closed-shell, which does not significantly change in this process. To treat this problem approximately, the electronic Hamiltonian $H_{\rm el}$ is replaced by the one-electron effective Hamiltonian:

$$h^e = -\frac{1}{2}\nabla^2 + V^e(r_C) - \frac{1}{r_H} \tag{58}$$

where r_C and r_H are respectively the electron distances to the C and H nuclei, and V^e is an effective potential that describes the interaction of of the active electron with the core $C^{4+}(1s^2)$.

A widely employed type of effective potentials are model potentials, and a simple example is that of ref. [54]:

$$V^e = -\frac{Z_C - N_c}{r} - \frac{N_c}{r_C}(1 + \alpha r_C)\exp(-\alpha' r_C) \tag{59}$$

where Z_C(=6) is the charge of the C nucleus, N_c the number of core electrons (2 in the present example) and α, α' two parameters, which are determined by fitting the $C^{3+}(1s^2 2s)$ and $C^{3+}(1s^2 2p)$ ionization potentials to the experimental values.

Some works have also treated systems with two active electrons, where the model potential describes the interaction of the active electrons with the atomic cores and the wavefunction for the active electrons is obtained by means of a CI calculation (see [55]). This method has been applied for example to $C^{3+}(1s^2 2s)$+ H(1s) collisions [56], where the CI calculation for the active electrons was carried out as explained in section 5.1.

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5.5. Calculation of dynamical couplings.

In general, the evaluation of rotational couplings is carried out analytically and it does not involves a special difficulty from the computational point of view (see [5]). Also, the switching function f that defines the CTF in eq. (39) is chosen in order to simplify the calculation of the new couplings introduced by the CTF. The main difficulty lies on the calculation of the radial couplings $\langle\psi_i|\frac{\partial}{\partial R}|\psi_j\rangle$, and there are two kinds of methods to evaluate them:

(i) *Analytical methods.* This includes methods based on the Hellman-Feynman theorem (see ref. [57]), which assume that the electronic wavefunctions ψ_j are exact eigenfunctions of H_{el}, and the methods of refs. [58, 59], which are not limited by this assumption. In particular, the method of ref. [58] has been employed for two-electron CI wavefunctions (see section 5.1 and 5.5) in terms of GTOs, where it is very useful because the radial couplings are expressed in terms of the derivatives with respect to R of the matrix elements H_{mn}, S_{mn} of eq. (49) that are analytical functions of R.

(ii) *Numerical methods.*
Although analytical methods, like that of ref. [58], are in principle the most appropriate for wavefunctions built from GTOs, their implementation in quantum chemistry packages involves a considerable programming effort, and numerical methods are usually employed. (see [60], [6]). These techniques are based on the finite difference differentiation approximation:

$$\left\langle \psi_i \left| \frac{\partial}{\partial R} \right| \psi_j \right\rangle \simeq \delta^{-1} \left\langle \psi_i(\boldsymbol{r}, R) | \psi_j(\boldsymbol{r}, R + \delta) \right\rangle \tag{60}$$

In general, the use of these numerical methods requires to check the stability with respect to the differentiation step δ. A practical disadvantage is the increase of the computational effort because the need of evaluating the wavefunctions in two nearby points R and $R+\delta$ and it is necessary to ensure that the sign of the wavefunctions is the same in both points.

6. Atomic expansions.

6.1. Basic equations.

At relatively high collision energies ($E \gtrsim 10$keV/a.m.u, for ion-H collisions), an atomic expansion becomes useful. A complete description of the method, together with references to many applications can be found in the book of ref. [1]. To describe the main characteristics of the atomic expansion, we consider the one-electron semiclassical equation (2), and we expand its solutions in the set of "travelling" AOs $\{\Phi_j^A D^A,\ \Phi_k^B D^B\}$ (see eqs. (4)-(9)):

$$\Psi^{AO}(\boldsymbol{r},t) = \sum_j a_j(t)\Phi_j^A(\boldsymbol{r}_A)D^A(\boldsymbol{r},t)\exp(-\mathrm{i}E_j^A t) + \\ + \sum_k a_k(t)\Phi_k^B(\boldsymbol{r}_B)D^B(\boldsymbol{r},t)\exp(-\mathrm{i}E_k^B t) \qquad (61)$$

where the AOs $\Phi_j^{A,B}$ are eigenfunctions of the atomic Hamiltonians $H^{A,B}$ of eqs. (6) and (10)

As in the molecular method, substitution of the expansion (61) yields a system of differential equations for the coefficients $a_j(t)$. However, the transitions between the AOs are mainly caused by electrostatic couplings of the form:

$$M_{ij}^{AB} = \int \Phi_i^{A*} H_{\mathrm{el}} \Phi_j^B \exp(-\mathrm{i}\boldsymbol{v}\cdot\boldsymbol{r})\mathrm{d}\boldsymbol{r} \qquad (62)$$

From the computational point of view, the presence of the quickly oscillating phase factor $(D^A)^* D^B = \exp(-\mathrm{i}\boldsymbol{v}\cdot\boldsymbol{r})$ in (62), makes difficult the evaluation of these integrals. Moreover, because of these phase factors, the integrals depend on b and v and must be calculated for each nuclear trajectory.

Atomic expansions have been applied in general to one-electron systems with some applications to two-electron systems (an example is the calculation for C^{3+}-H of ref. [61]). For many-electron systems, the calculations are based on the use of the independent electron approximation [62], and a detailed example of this kind of calculations can be found in ref. [11].

6.2. Pseudostates.

The atomic expansion is usually employed in a region of impact energies where ionization starts to be competitive with charge exchange and excitation processes. Therefore, many works have studied the extension of expansion (61) to describe the ionization continuum; this is often carried out by adding to this expansion the so-called *pseudostates*. To introduce these pseudostates, we consider a two-centre basis set (e.g. STOs) $\{\xi_s^{A,B}\}$, similar to that of eq. (52), which is used to obtain approximations to the AO $\Phi_k^{A,B}$. We write

$$\Phi_k^{A,B} = \sum_s b_{sk}^{A,B} \xi_s^{A,B} \tag{63}$$

The coefficients $b_{sk}^{A,B}$ are then evaluated variationally; namely, they are solutions of the secular equations :

$$(\boldsymbol{H^{A,B}} - \overline{E_j^{A,B}} \boldsymbol{S^{A,B}}) \boldsymbol{b_j^{A,B}} = 0 \ , \tag{64}$$

which are analogous to the equation (48) of section 5.1 but for a one-electron atomic case. The elements of the matrices $\boldsymbol{H^{A,B}}$ and $\boldsymbol{S^{A,B}}$ are

$$H_{st}^{A,B} = \left\langle \xi_s^{A,B} | H^{A,B} | \xi_t^{A,B} \right\rangle \ ; \ \ S_{st}^{A,B} = \left\langle \xi_s^{A,B} | \xi_t^{A,B} \right\rangle \tag{65}$$

The solutions of (64) with $\overline{E_j^{A,B}} < 0$ are approximations to the AOs, while those with $\overline{E_j^{A,B}} > 0$ are approximations to the continuum states, called pseudostates. Their inclusion in the expansion, together with a set of bound states, has the following practical consequences:

(i) Since the pseudostates complete the basis set, delocalization effects are better represented in the the augmented basis. Therefore their inclusion makes it possible to extend the treatment to low energies.

(ii) The pseudostates furnish a representation of the ionizing flux through transitions from the bound AO to the pseudostates. This implies that the populations of the bound AOs are also improved, and therefore the values of charge transfer and excitation cross sections.

(iii) One can calculate ionization cross sections; these are approximated by the sum of the cross sections for transitions to the pseudostates.

Atomic calculations with pseudostates have been carried out with one-centre basis, formed for example by orbitals of the target atom $\{\Phi_A\}$. If the origin of electronic coordinates is on the nucleus A then $p = 0$ and $D^A \equiv 0$ (see fig.1 and eq. (4)), and the expansion has the form:

$$\Psi^{OC}(\boldsymbol{r}, t) = \sum_j aj(t) \Phi_j^A(\boldsymbol{r}_A) \exp(-\mathrm{i} E_j^A t) \ , \tag{66}$$

which simplifies the calculation of the required matrix elements. This kind of expansion can include a set of pseudostates, which represent continuum states and also charge transfer (with the corresponding ETF). A systematic method to build up these pseudostates, applied in several papers of the Frankfurt group, is the basis generator method, (see [63, 64, 11]) where a set of pseudostates $\{\Phi_j^\mu\}$ is created by repeated application of the operator $[H_{\mathrm{el}} - \mathrm{i}\partial/\partial t]$ [65] on a set of one-centre AOs $\{\Phi_j^A\}$:

$$\Phi_j^\mu = [H_{\mathrm{el}} - \mathrm{i}\partial/\partial t]^\mu \Phi_j^A \tag{67}$$

In this way, the electronic flux leaving the zeroth order functions (the AO, Φ_j^A) is absorbed by the first order pseudostates Φ_j^1. The second order pseudostates Φ_j^2 absorb the flux that leaks the first-order ones and does not come back to the original functions, and so on (see [36]). The decreasing populations of increasing hierarchy absorber states provides a check of the convergence of this procedure. An obvious practical difficulty in the application of this scheme is the possible redundances between absorber states, which leads, after orthogonalization of the set, to vanishing functions. Another difficulty is related to the Coulomb singularity in the potential Z_B/r_B, which is solved by using regularized potentials (see [66]). Finally, the solutions must be projected on the physical charge transfer states of (8) to obtain charge transfer cross sections, and it is in general difficult to separate charge transfer from ionization.

Two-center AO calculations employ expansion (61) with pseudostates centered in one or both nuclei. An illustration of state-of-the-art atomic ([67], [68])and molecular [69] calculations is shown in fig. 3 for the particular case of C^{4+}+ H collisions (see section 5.4). The excelent agreement between calculations using different methods indicates that CC calculations for (quasi)one-electron systems can be more accurate than the experimental results.

Three-center bases have been also used to define pseudostates [70, 71]. A CC three-center expansion has the form (see e.g. [72]):

$$\Psi^{TC}(\boldsymbol{r},t) = D^A \sum_j aj(t)\Phi_j^A(\boldsymbol{r}_A)\exp(-\mathrm{i}E_j^A t) +$$

$$+D^B \sum_k a_k(t)\Phi_k^B(\boldsymbol{r}_B)\exp(-\mathrm{i}E_k^B t) + D^C \sum_l a_l(t)\Phi_l^C(\boldsymbol{r}_B)\exp(-\mathrm{i}E_l^C t) \quad (68)$$

where Φ_l^C are orbitals centred in an intermediate point C of the internuclear axis and the ETF $D^C(\boldsymbol{r},t)$ represents the translational motion of an electron with the velocity of the point C with respect to the coordinates origin. The inclusion of the third center basis functions is based on the physical picture of ionization at low v (see [73]) in which the electron is not able to follow the motion of the fast nuclei and remains between them, which is also the basis of the definition of the molecular pseudostates of ref. [35].

7. Extension to ion-H_2 collisions.

The methods explained in the preceeding sections can be extended to treat ion-molecule collisions. In particular, at low impact energies, CC molecular expansions are used and the rotational motion is described by means of the sudden approximation; this is the basis of the so-called infinite order sudden approximation (IOSA), where a full quantal treatment is employed (see [77]). For $E \gtrsim$50eV/a.m.u., the semiclassical method with three-centre molecular expansion is employed, which is described in this section. Only a few works have tried to extend the atomic CC expansion ([78], [79], [80]), where the target molecule is approximated by means of a spherically symmetric effective potential. Classical trajectory Monte Carlo methods have been also applied (see e.g. [81] and references therein). At high energies the calculations use the sudden approximation for the ro-vibrational motion, which is explained in section 7.2 and in many cases the

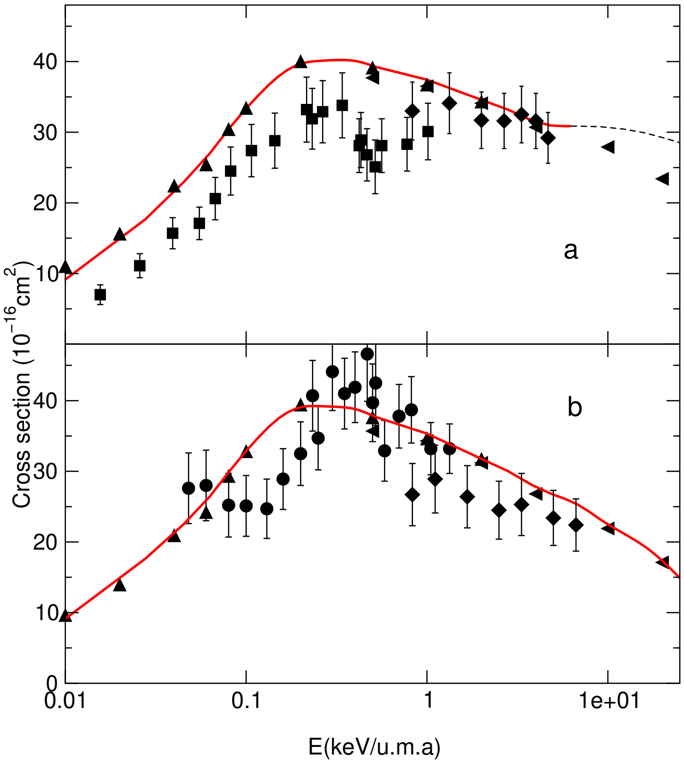

Figure 3. (a) Total electron capture cross section in C^{4+}+ H(1s) collisions: Full curve, [69]; ▲,[68] with rectilinear trajectories; ◁, [67]. Experimental results: ♦, [74]; ■, [75]. (b) Cross section for electron capture into C^{3+}(n=3): Full curve, [69]; ▲,[68] with rectilinear trajectories; ♦, [74]; ● [76].

Franck-Condon approximation, which can be obtained as an additional approximation to the sudden vibrational approach.

7.1. Close-coupling treatment.

To describe the main features of the CC treatment of ion-H_2 collisions, we consider the electron capture:

$$X^{q+} + H_2 \to X^{(q-1)+} + H_2^+ \tag{69}$$

and excitation

$$X^{q+} + H_2 \to X^{q+} + (H_2)^* \tag{70}$$

processes, where the products of these reactions can be found in electronic or vibrational excited states. Here we do not consider processes leading to either electronic or vibrational dissociative states.

In the semiclassical approach, the ion-diatomic relative motion is described with straight-line trajectories $\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t$, where $\boldsymbol{R}$ is the ion position vector with respect to the centre of the H_2 internuclear axis (see fig. 4). The remaining degrees of freedom

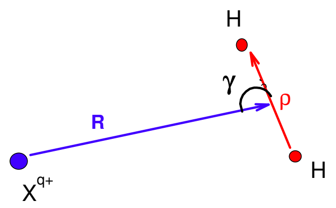

Figure 4.

are treated quantally, and the corresponding wavefunction $\Psi(\boldsymbol{r},\boldsymbol{\rho},t)$ is solution of the semiclassical equation:

$$\left(H_{\mathrm{i}} - \mathrm{i}\,\frac{\partial}{\partial t}\bigg|_{\boldsymbol{r},\boldsymbol{\rho}} \right) \Psi(\boldsymbol{r},\boldsymbol{\rho},t) = 0 \tag{71}$$

where $\boldsymbol{\rho}$ is the target internuclear vector in the laboratory frame (see fig. 5), and $\boldsymbol{r}$ denotes the coordinates of all electrons. The equation (71) is the equivalent of (2) for ion-diatomic collisions. In this equation, H_{i} is the total Hamiltonian of the three-centre system without the kinetic energy term asociated to the nuclear motion along the coordinate $\boldsymbol{R}$ that is treated classicaly. Explicitly:

$$H_{\mathrm{i}}(\boldsymbol{r},\boldsymbol{R},\boldsymbol{\rho}) = -\frac{1}{2\mu}\nabla^2_{\rho} + H_{\mathrm{el}} \tag{72}$$

where μ is the H_2 reduced nuclear mass and

$$H_{\mathrm{el}}(\boldsymbol{r}_1,\boldsymbol{r}_2,...,\boldsymbol{r}_N,R,\rho,\gamma) = \sum_{i=1}^{N}(T_i+V_i) + \sum_{j<k}^{N}\frac{1}{r_{jk}} + V_{\mathrm{nuc}}\ , \tag{73}$$

being γ the angle between vectors $\boldsymbol{R}$ and $\boldsymbol{\rho}$, T_i the electronic kinetic energy operators, V_i the attraction potential of electron i by the three nuclei, and V_{nuc} the nuclear repulsion potential.

The equation (71) must be solved with the initial condition:

$$\Psi \underset{t\,\to\,-\infty}{\sim} \Psi^{JM}_{i\mu} = \rho^{-1}Y_{JM}(\widehat{\boldsymbol{\rho}})\psi_{i\mu}(\boldsymbol{r},\rho,t) \tag{74}$$

with

$$\psi_{i\mu} = \Phi_i(\boldsymbol{r};\rho)\chi_{i\mu}(\rho)D^i(\boldsymbol{r},t)\exp(-\mathrm{i}E_it) \tag{75}$$

where Y_{JM} is the spherical harmonic that corresponds to the H_2 initial rotational state, D^i is a plane-wave translation factor, $\chi_{i\mu}$ is the wavefunction for the H_2 vibrational initial state and Φ_i is the electronic initial state, which is the product of the initial electronic states of the ion X^{q+} and the H_2 molecule:

$$\Phi_i(\boldsymbol{r},\rho) = \Phi_i^{\mathrm{H}_2}(\boldsymbol{r}_1,\boldsymbol{r}_2;\rho)\Phi_i^{\mathrm{X}}(\boldsymbol{r}_3,...,\boldsymbol{r}_N) \tag{76}$$

Analogously, a reaction exit channel has the form:

$$\Psi^{J'M'}_{n\nu} = \rho^{-1}Y_{J'M'}(\widehat{\boldsymbol{\rho}})\psi_{n\nu} \tag{77}$$

with

$$\psi_{n\nu} = \Phi_n(\boldsymbol{r};\rho)\chi_{n\nu}(\rho)D^n(\boldsymbol{r},t)\exp(-\mathrm{i}E_f t) \tag{78}$$

For electronic and vibrational excitation processes , $\chi_{n\nu}$ is a H_2 vibrational wavefunction and

$$\Phi_n(\boldsymbol{r},\rho) = \Phi_n^{\mathrm{H}_2}(\boldsymbol{r}_1,\boldsymbol{r}_2;\rho)\Phi_n^{\mathrm{X}}(\boldsymbol{r}_3,...,\boldsymbol{r}_N)\,, \tag{79}$$

while for electron capture, $\chi_{n\nu}$ is a vibrational function of H_2^+ and

$$\Phi_n(\boldsymbol{r},\rho) = \Phi_n^{\mathrm{H}_2^+}(\boldsymbol{r}_1;\rho)\Phi_n^{\mathrm{X}}(\boldsymbol{r}_2,...,\boldsymbol{r}_N)\,, \tag{80}$$

In the range of impact energies E >50eV/a.m.u., we can consider that the characteristic collision period is short compared to the rotation period of the diatomic molecule and use the *sudden approximation* for rotation. In this approximation, we assume that the rotational component of the the collisional wavefunction does not change during the collision, and accordingly we write:

$$\Psi = \rho^{-1}Y_{JM}(\widehat{\boldsymbol{\rho}})\psi(\boldsymbol{r},\boldsymbol{\rho},t) \tag{81}$$

It can be shown (see ref. [82]) that assuming that all the M values are equally probable in the initial condition, the probability for transition to all rotational states of a given vibronic state $\psi_{n\mu}$, can be expressed as an orientation averaged magnitude:

$$\mathcal{P}_{n\nu}(\boldsymbol{b},v) = (4\pi)^{-1}\int \mathrm{d}\widehat{\boldsymbol{\rho}}\,P_{n\nu}(\widehat{\boldsymbol{\rho}},\boldsymbol{b},v) \tag{82}$$

where

$$P_{n\nu}(\widehat{\boldsymbol{\rho}},\boldsymbol{b},v) = \lim_{t\to\infty}\left|\langle\psi_{n\nu}|\psi\rangle_{\boldsymbol{r},\rho}\right|^2 \tag{83}$$

is the transition probability for a fixed orientation of the H-H internuclear axis with respect to the direction of $\boldsymbol{v}$. The corresponding orientation averaged cross sections for transition to the vibronic state $\psi_{n\nu}$ is

$$\sigma_{n\nu}(v) = \int \mathrm{d}\boldsymbol{b}\mathcal{P}_{n\nu}(\boldsymbol{b},v) = (4\pi)^{-1}\int \mathrm{d}\widehat{\boldsymbol{\rho}}\int P_{n\nu}(\widehat{\boldsymbol{\rho}},\boldsymbol{b},v)\mathrm{d}\boldsymbol{b} \tag{84}$$

The CC method can be applied to the function ψ, which is expanded in the vibronic basis $\{\phi_j(\boldsymbol{r};\boldsymbol{R},\boldsymbol{\rho})\chi_{j\nu}(\rho)\}$. Explicitly:

$$\psi = D(\boldsymbol{r},t)\sum_j\sum_\nu a_{j\nu}(t;\widehat{\boldsymbol{\rho}},\boldsymbol{b},v)\phi_j\chi_{j\nu}\exp\left[-\mathrm{i}\int_0^t(\varepsilon_j(R,\gamma)+\epsilon_{j\nu})\mathrm{d}t'\right] \tag{85}$$

where D is a CTF, $\phi_j(\boldsymbol{r};\rho,R,\gamma)$ are the electronic wavefunctions, which are (approximate) solutions of the fixed nuclei Schrödinger equation (the analogous to eq. (15) for the three-centre problem):

$$H_{\mathrm{el}}(\boldsymbol{r};\,\rho,R,\gamma)\phi_j(\boldsymbol{r};\,\rho,R,\gamma) = \varepsilon_j(\rho,R,\gamma)\phi_j(\boldsymbol{r};\,\rho,R,\gamma) \tag{86}$$

As for ion-atom collisions, diabatic basis sets can be employed (see section 3.3), where functions ϕ_j are not solutions of (86) (see [77]). The vibrational wavefunctions $\chi_{j\nu}(\rho)$ can be defined in several ways, but the simplest choice, which fulfills the asymptotic conditions (75) and (78), is to multiply each electronic state ϕ_j by the vibrational functions $\chi_{j\nu}$ that correspond to either H_2 or H_2^+ molecules depending on the asymptotic structure of this electronic state. They are solutions of the equations:

$$\left[-\frac{1}{2\mu}\nabla_\rho^2 + \varepsilon_j(\rho, R=\infty) - \varepsilon_j(\rho_{0j}, R=\infty)\right]\chi_{j\nu}(\rho) = \epsilon_{j\nu}\chi_{j\nu}(\rho) \qquad (87)$$

with ρ_{0j} the equilibrium internuclear separation of the diatomic molecule in the electronic state j.

Substitution of eq. (85) in (71) leads to a system of differential equations for the coefficients $a_{j\nu}$, from which one can calculate the transition probabilities and cross sections of eqs. (83) and (84) in a similar way to the ion-atom case. However, the problem is very complex from the computational point of view. It involves:

(i) Evaluation of potential energy surfaces ε_j and dynamical couplings, which are now functions of three variables R, ρ, γ (they only depend on R in the ion-atom case).

(ii) Calculation of a set of vibrational functions and evaluation of the dynamical couplings in the vibronic basis:

$$\left\langle \phi_j\chi_{j\nu}D|H_{\rm i} - {\rm i}\frac{\partial}{\partial t}|\phi_k\chi_{k\mu}D\right\rangle_{\boldsymbol{r},\rho}$$

A large number of coupled channels can be involved when using the vibronic expansion (85). In fact, including only bound vibrational states of H_2 and H_2^+ and six electronic states, the vibronic basis includes about 100 functions.

(iii) Solution of the system of differential equations for different orientations of the diatom and integration (eq. (84)) of the transition probabilities to obtain the corresponding cross sections

A reason for the complexity of ion-molecule collisions is the anisotropy of the interaction potential . In particular, when using the expansion (85), potential energy surfaces and dynamical couplings depend on the angle γ (see fig. 4), which changes along the trajectory. To simplify the calculation, an additional *isotropic* approximation can be introduced by substituting energies and couplings calculated at a fixed molecular orientation, γ_0, which leads to the isotropic transition probabilities $P_{n\nu}^{\rm iso}(\boldsymbol{b}, v; \gamma_0)$ and cross sections, $\sigma_{n\nu}^{\rm iso}(v;\gamma_0)$. The ensuing average over γ_0 yields the corresponding orientation averaged cross sections:

$$\sigma_{n\nu}(v) \simeq \int_0^{\pi/2} {\rm d}\gamma_0 \sin\gamma_0 \sigma_{n\nu}^{\rm iso}(v;\gamma_0) \qquad (88)$$

This is the approach generally employed in IOSA calculations [77]. In a drastic approximation the orientation average cross section $\sigma_{n\nu}(v)$ is replaced by the corresponding isotropic result for a given γ_0, $\sigma_{n\nu}^{\rm iso}(v;\gamma_0)$.

Until now, only a few works [83] have considered the validity of the isotropic approximation. In general, charge transfer in collisions of multiply-charged ions with H_2 (see e.g. results for C^{4+}-H_2 of ref. [84]) take place in the neighborhood of avoided crossings of the potential energy surfaces at relatively large internuclear distances where anisotropy effects are unimportant, and $\sigma_{n\nu}^{\rm iso}(v;\gamma_0)$ is practically independent on γ_0. On the other hand, collisions of singly charged ions (Li^+, H^+) with H_2 take place at shorter R and the dependence of $\sigma_{n\nu}^{\rm iso}(v;\gamma_0)$ on γ_0 is noticeable for energies $E \lesssim 250$eV/a.m.u.. However, results of refs. [83] show that this dependence cancels out when the cross sections are averaged over the molecular orientation with good agreement between cross sections calculated using eq. (88) and the more exact values from eq. (84), and that even good agreement is found with $\sigma_{n\nu}^{\rm iso}(v;\gamma_0)$ an intermediate angle $\gamma_0 \simeq 60^0$.

7.2. The sudden vibrational approximation

Because of the complexity of ion-molecule collisions, some additional approximations have been proposed, which are particularly useful when v increases, because of the very large vibronic basis set required. In particular, when the vibrational period is larger than the time interval in which electronic transitions take place, one can use the sudden approximation for vibration (see ref.[17]) where it is assumed that the initial vibrational wavefunction $\chi_{i\mu}$ remains unchanged during the collision. So that, the CC wavefunction is substituted by:

$$\psi = D(\boldsymbol{r},t)\chi_{i\mu}\sum_j a_j(t;\boldsymbol{\rho},\boldsymbol{b},v)\phi_j \exp\left[-\mathrm{i}\int_0^t \varepsilon_j(R,\gamma)\mathrm{d}t'\right] \tag{89}$$

This is the basis of the SEIKON method of ref.[82], where it was shown that the transition probabilities are:

$$P_{n\nu}(\widehat{\boldsymbol{\rho}},\boldsymbol{b},v) = \left|\int \mathrm{d}\rho\chi_{i\mu}\chi_{n\nu}\exp\left[\int_0^\infty \mathrm{d}t(\varepsilon_n - E_n)\right] a_n(t=\infty;\boldsymbol{\rho},\boldsymbol{b},v)\right|^2 \tag{90}$$

Although the SEIKON approach notably simplifies the calculation with respect to the vibronic CC method, it still involves a considerable computational effort. In particular, for a given trajectory and molecular orientation $\widehat{\boldsymbol{\rho}}$, it requires:

- Calculation of potential energy surfaces and dynamical couplings for a grid of values of R, ρ and γ, and 2D interpolation of these molecular data as functions of R and γ
- Integration for each value of ρ of a system of differential equation to obtain the coefficients a_n.
- Integration of eq. (90) to evaluate the transition probabilities $P_{n\nu}$.

The SEIKON method has been successfully applied to several collisions, and, as an example, we show in fig. 5 the results [21] for electron capture into individual vibrational states in the process

$$\mathrm{C}^{2+}(2\mathrm{s}2\mathrm{p};{}^3\mathrm{P}) + \mathrm{H}_2(\mathrm{X}^1\Sigma_g^+,\nu=0) \rightarrow \mathrm{C}^+(2\mathrm{s}2\mathrm{p}^2;{}^2\mathrm{D}) + \mathrm{H}_2^+(\mathrm{X}^2\Sigma_g^+,\nu) \tag{91}$$

compared to the experimental results of [85], which shows the accuracy of this method.

An additional approximation is obtained by assuming that the coefficients a_n can be taken as constants in the interval of ρ where the vibrational functions $\chi_{i\mu}$, $\chi_{n\nu}$

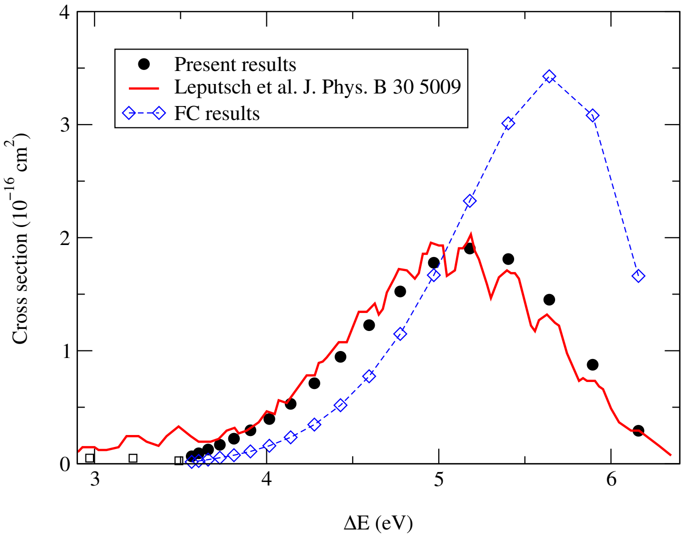

Figure 5. Comparison of electron capture cross sections into individual H_2^+ vibrational for the reaction (91): • Calculations from ref. [21] using SEIKON ⋄ FC results. Line, experimental results from ref.[85]

have appreciable values. If we take the values of the coefficients at the equilibrium internuclear distance of the initial electronic state ρ_{0i}, we obtain:

$$P_{n\nu} = \left| \int \mathrm{d}\rho \chi_{i\mu}\chi_{n\nu} \right|^2 |a_n(t=\infty; \boldsymbol{\rho_{0i}}, \boldsymbol{b}, v)|^2 \ , \qquad (92)$$

which is the familiar Franck-Condon (FC) approximation. The FC approximation only requires to calculate the coefficients a_n for a single value of ρ and is then much simpler than the vibrational sudden approximation from the computational point of view.

In general, the FC approximation becomes more accurate as v increases, but there is a reduced experience in comparing FC results with the more accurate ones obtained by applying (89) and (90) (see [21] and references therein). These results indicate that the FC approximation is appropriate to evaluate total cross sections at E larger than about 500 eV/a.m.u., but important disagreements have been found for partial cross sections, in particular for vibrational distributions, as can be observed in the illustration of fig. 5.

In a recent work, [86] we have studied the low v limit of the SEIKON method by comparing total cross sections calculated by employing this approximation with those obtained from the vibronic CC expansion (eq. (85)) for the benchmark collisions:

$$\mathrm{H}^+ + \mathrm{H}_2(X^1\Sigma_g^+, \nu = 0) \rightarrow \mathrm{H}(1\mathrm{s} + \mathrm{H}_2^(X^2\Sigma_g^+, \nu') \qquad (93)$$

and

$$\mathrm{H}^+ + \mathrm{H}_2(X^1\Sigma_g^+, \nu = 0) \rightarrow \mathrm{H}^+ + \mathrm{H}_2(X^1\Sigma_g^+, \nu') \qquad (94)$$

The calculations show (see fig.6) an important disagreement between the total charge transfer cross sections calculated with both methods for E <250 eV/amu,

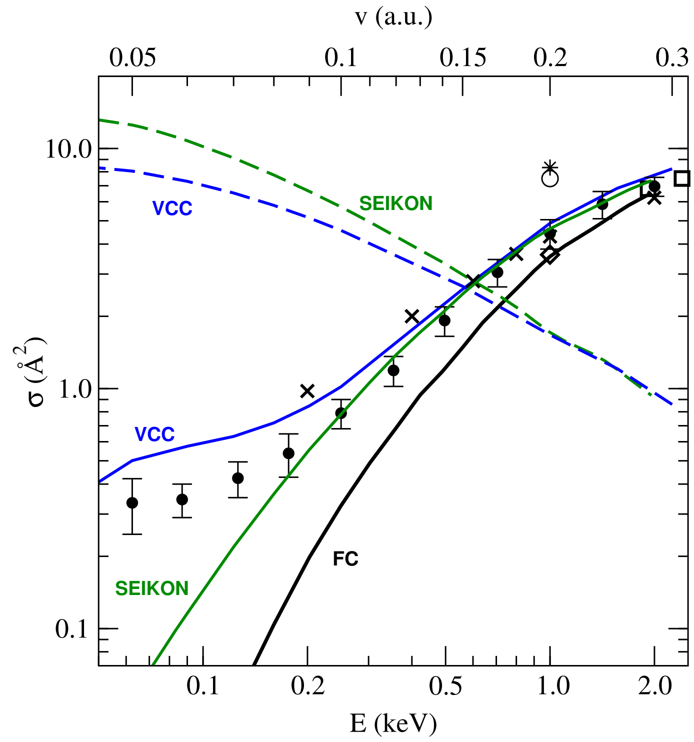

Figure 6. Cross sections for H^{+}+H_2 collisions. Lines, results of ref. [86](VCC, vibronic close-coupling; SEIKON: vibrational sudden; FC, Franck-Condon). Solid lines and symbols: charge transfer (Eq. 93); dashed lines: vibrational excitation (Eq. 94). ×, [88] multiplied by 2 following author's suggestion. Experiments: •, [89]; ◇, [90]; ◯, [91]; ⋆, [92].

indicating a limitation of the SEIKON approach. The analysis of ref. [86] has pointed out that there are two mechanisms leading to the charge transfer process:

- At $E \gtrsim 250$eV, the charge transfer process takes place through direct transitions from the the entrance channel to the charge transfer ones.
- At $E \leq 250$eV, the reaction (93) takes place through a two-stage mechanism first suggested in ref. [87]. It involves the vibrational excitation to H_2 levels with $\nu \simeq 4$ followed by transitions from those states to the quasidegenerate charge transfer state with $\nu' = 0$ in the outgoing part of the collision.

The low-v mechanism cannot be reproduced by employing the sudden vibrational approximation, which explains the limitation of the SEIKON calculation. However, since this limitation is mainly a consequence of the quasidegeneracy of the vibronic levels in H^{+}- H_2, further work is needed to know the limitations of the method for other systems.

8. Concluding remarks

In this chapter we have described the main characteristics of CC treatments of ion-atom and ion-molecule collisions. We can summarize the present situation with regards to the practical application of these methods as follows:

1. Low energy ion-atom collisions are generally described using molecular CC expansions. These methods are well established for single-electron systems at low velocities ($v \lesssim v_0$) where ionization is not important. In particular, the computing facilities allow to employ relatively large expansions, for which the choice of ETFs is not critical. As an example, electron capture cross sections for collisions between fully stripped ions and hydrogen atoms were calculated in ref. [93], using basis sets that include about 100 molecular functions multiplied by a common translation factor. At higher v new techniques are needed to describe ionization.
2. In the last ten years, several calculations have considered many electron ion-atom systems by using quantum chemistry ab initio packages. This work has been motivated by state selective measurements [94] which in many cases involve the contamination of the initial beam by unknown amounts of metastable ions. Although the theoretical methods are similar to that employed in single electron systems, the application is not a routine work, which explains the necessity of calculations for these systems.
3. Because of the complexity of ion-molecule collisions, relatively few calculations have been performed for these systems. In practice, methods based on the use of the sudden approximation are applied. Although a first study has been recently presented for the benchmark system H^++ H_2 [86], further work is required to know the energy limits of these approximations. The study of anisotropy effects is also needed in particular in relation to recent experiments [95], where the dissociation of molecules after collisions with ions has been studied as function of the molecular orientation. Finally, data for collisions more complex molecules are required in view of possible applications in fusion research and astrophysics.

Acknowledgments

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