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Schwinger variational approach to excitation of hydrogen atoms by protons impacts at intermediate energies

Presented by :

Bahloul Meriem

Thesis defended on 22/06/2025, before the jury composed of:

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To my 17-year-old self, I'm sorry for not becoming the person you hoped we'd grow into. This is for you; I'll never stop trying.

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"Study hard what interests you the most in the most undisciplined, irreverent, and original manner possible."

Richard Feynman

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In the name of Allah, the Most Gracious, the Most Merciful

"And We are closer to him than [his] jugular vein."
Surah Qaf, 50:16

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"Allah does not burden a soul beyond what it can bear."
Surah Al-Baqarah, 2:286

ملخص

في إطار تقريب معامل الاصطدام، تم تطبيق المقاربة التغايرية المبنية على الصيغة الكسرية لمبدأ شوينغر التغايري من أجل حساب المقاطع العرضية الكلية للإثارة المباشرة لذرة الهيدروجين نحو المستويين $n = 2$ و $n = 3$ تحت تأثير تصادمات البروتونات (H^{+}). أُنجزت الدراسة ضمن نطاق طاقوي يتراوح بين 1 keV و 200 keV، شاملاً مجال الطاقات المتوسطة حول 50 keV. أظهرت النتائج النظرية توافقاً جيداً مع مختلف المعطيات التجريبية المتوفرة، لا سيما تلك الخاصة بـ .Park et al و .Barnett et al، بالإضافة إلى عدة نماذج نظرية مثل TCES, POHC, UOHC, SCE, TDSE, TCAO.

الكلمات المفتاحية: التصادمات الذرية، مبدأ شوينغر التغايري، الإثارة الذرية، المقاطع العرضية.

Abstract

Within the framework of the impact parameter formalism, the variational approach based on the fractional form of the Schwinger variational principle is applied to evaluate the total cross sections for the direct excitation of the hydrogen atom to the states $n = 2$ and $n = 3$ by proton (H^{+}) impact. The study was conducted in the energy range from 1 keV to 200 keV, including the intermediate energy domain around 50 keV. Our theoretical predictions are in good agreement with the various available experimental results, particularly those of Park et al. and Barnett et al., as well as with several theoretical models such as TCES, POHC, UOHC, SCE, TDSE, and TCAO.

Keywords: Atomic collisions, Schwinger variational principle, Atomic excitation, Cross sections

Résumé

Dans le cadre du formalisme du paramètre d'impact, l'approche variationnelle basée sur la forme fractionnaire du principe variationnel de Schwinger est appliquée pour l'évaluation des sections efficaces totales d'excitation directe de l'atome d'hydrogène vers les états $n = 2$ et $n = 3$ par impact de protons (H^{+}). L'étude a été réalisée dans la gamme d'énergie allant de 1 keV à 200 keV, incluant le domaine des énergies intermédiaires autour de 50 keV. Nos prédictions théoriques sont en bon accord avec les différentes données expérimentales disponibles, notamment celles de Park et al. et de Barnett et al., ainsi qu'avec plusieurs modèles théoriques comme TCES, POHC, UOHC, SCE, TDSE et TCAO.

Mots clés : Collisions atomiques, Principe variationnel de Schwinger, Excitation atomique, Sections efficaces

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List of Abbreviations

Abbreviation	Meaning
Born-I	First-order Born approximation
Born-II	Second-order Born approximation
CDW	Continuum Distorted Wave
CDW-EIS	Continuum-Distorted-Wave Eikonal Initial State
CPT	Classical Perturbation Theory
DWBA	Distorted Wave Born Approximation
Hα	Balmer-alpha emission line (transition $n = 3 \to n = 2$)
LCAO	Linear Combination of Atomic Orbitals
OHCE	One and Half Centred Expansion
PWBA	Plane-Wave Born Approximation
R-matrix	Variational method for collision theory
SCE	Single-Centred Expansion
Schw 5	Schwinger method with 5 basis states
Schw 10	Schwinger method with 10 basis states
TCAO	Two-Centred Atomic Orbital Expansion
TCE	Triple Centre Expansion
TDSE	Time-Dependent Schrödinger Equation
TCES	Two-Center Expansion Sturmian approach
UOHC	Unitary One-Half-Centered method
VPS	Vainshtein-Presnyakov-Sobelman approximation
σ(Hα)	Cross section for Hα emission
Π(Hα)	Polarization fraction of Hα emission
Z_P, Z_C	Nuclear charges of projectile and target
v_p, v_e	Velocities of projectile and electron

General Introduction

Atomic collisions concern the study of phenomena induced by the relative motion of charged particles (atoms, ions, electrons, etc.) in interaction. Elementary processes such as excitation, ionization, and electron transfer arising in atomic collisions have attracted great interest for a long time. A considerable amount of theoretical work has been devoted to the study and understanding of the scattering of atoms and ions [9, 40].

The proton–hydrogen collision remains a reference for the development of new atomic scattering theories. There are three primary inelastic processes: target excitation, electron capture by the projectile, and direct ionization.

The study of these fundamental processes of atomic collision between the proton and the hydrogen atom is of great interest in various branches of physics, including astrophysical plasmas and the physics of thermonuclear fusion plasmas.

At intermediate collision energies, the three inelastic processes — excitation, electron capture, and ionization — can occur with comparable probabilities [17] and thus must be treated simultaneously. While the Close-Coupling approximation has been applied to address this, the results remain inconclusive and sometimes unsatisfactory. Indeed, in this energy region, the behaviour of the electronic wave function becomes more complex than at low energy (where transfer dominates) or at high energy (where excitation and ionization are predominant). The scattering wave function must therefore represent all these processes at the same time, which is a major theoretical difficulty.

One of the most promising approaches is the Schwinger variational principle, which offers a rigorous and non-perturbative mathematical framework for approximating scattering amplitudes.

In order to investigate the direct electronic excitation of hydrogen-like atoms by impact of ions at intermediate velocities, this variational approach was introduced [7, 18]. Even when helium-like ions impinging on different rare gases were excited at 400 MeV $Fe^{24+}(1s^2)$ [63], 34 MeV/nucleon Kr^{34+} [11], and 13.6 MeV/u $Ar^{16+}(1s^2)$ [1], it was demonstrated to be highly effective in forecasting the saturation of cross sections when the projectile charge was raised. However, due to neutral projectiles, these results were achieved by ignoring the interaction between excitation and capture channels.

In the case of the excitation of a hydrogen atom by proton impacts at intermediate and low velocities, it should not be possible to ignore the coupling between excitation and capture channels. The objective of this study is to apply a fractional form of the Schwinger variational principle to compute total excitation cross sections of the hydrogen atom induced by proton impact in the intermediate energy domain target in the cross sections. Specifically, we aim to analyze transitions to the $n = 2$ and $n = 3$ excited states, using basis sets of increasing complexity (ranging from 5 to 14 states) to assess convergence and accuracy. Our results are critically compared with experimental data—such as those of Park et al. and Barnett et al.—and with outcomes from other theoretical models, including the Close-Coupling, Time-Dependent Schrödinger Equation (TDSE), and Sturmian Two-Center Expansion (TCES) approaches. The rationale for this work is twofold:

- **First**, to demonstrate the effectiveness of the Schwinger variational method in resolving the longstanding inconsistencies in intermediate-energy excitation cross sections.
- **Second**, to provide a benchmark dataset that can be used to validate or challenge existing theoretical and experimental results.

By doing so, this study contributes to the refinement of collision models and advances our understanding of ion-atom interaction dynamics.
This thesis is organized as follows:

- **Chapter 1** presents the theoretical foundations of ion-atom collision processes and surveys existing approaches.
- **Chapter 2** introduces the Schwinger variational formalism and details the derivation of the fractional amplitude expression.
- **Chapter 3** describes the numerical implementation and outlines the basis sets used.
- **Chapter 4** presents and discusses the results of our calculations, followed by a comparison with existing theoretical and experimental data.
- **Appendices** provide supplementary derivations and detailed tabulations of the matrix elements and cross-section results.

This thesis concludes with a general conclusion and some suggestions regarding the work.

Chapter 1

Theoretical Foundations of Atomic Collisions

1.1 Fundamental collision processes:

During ion-atom collisions, a portion of the kinetic energy of motion is transferred to both electron clouds, leading to a rearrangement of the states of one or more electrons, corresponding to processes such as excitation, ionization, or capture (Figure 1.1). [1]

1.1.1 Direct Single-Electron Processes:

In the study of collisions between a projectile ion P and an atomic or molecular target$T$, the "active" electrons of the target are those that, during the interaction, can undergo transitions from an initial orbital T to another orbital within T (excitation), to the continuum (ionization), or to an orbital of P (capture). Conversely, "passive" electrons are those that retain their quantum states throughout the collision.

To facilitate the analysis of these three fundamental processes, a single-electron model is adopted, wherein the concept of an "active electron" serves to characterize single-electron processes and define the relevant impact velocity regimes.

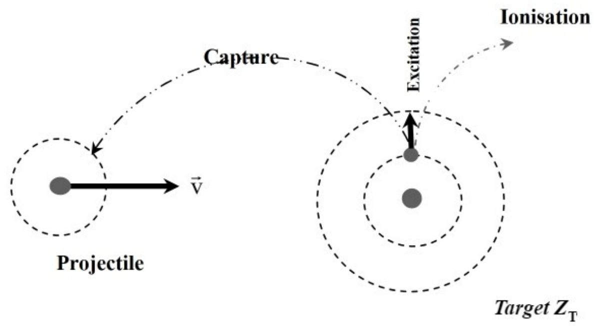

Figure 1.1: Collision system.

1.1.1.1 Ionization:

In this process, the interaction is sufficiently intense, resulting in substantial energy transfer. As a consequence, the transferred energy may be sufficient to dislodge an electron from the target atom$T$, leading to the formation of an ion-electron pair (a positively charged ion and a free electron) within the medium.

1.1.1.2 Excitation:

In contrast, if the interaction is insufficient to induce the ionization, only excitation occurs, wherein the electron undergoes a transition from an initial quantum state to a less tightly bound final state. This process is relatively unlikely for biological targets.

1.1.1.3 Capture:

The single capture process refers to the relocation of an electron from a bound state of the target atom T to a bound state of the projectile P without the simultaneous emission of radiation. This phenomenon, also known as charge transfer, is particularly significant in the context of heavy-ion collision dynamics.

1.2 Impact velocity regimes:

For each collision system, these various processes are characterized by cross-sections that, for a given projectile ion and target, depend on the collision energy, as shown in figure (I-2) for the case of a proton in a hydrogen system. According to the speed of the projectile

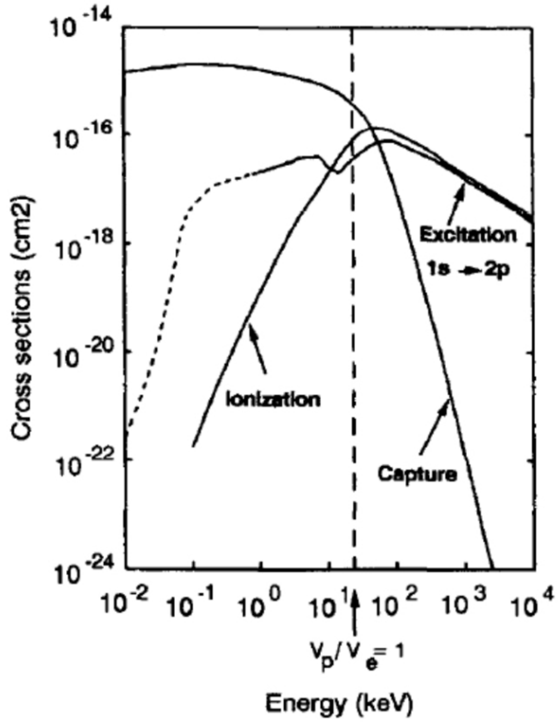

Figure 1.2: Capture, excitation, and ionization cross sections as a function of energy for p + H collisions. Extracted from Vernhet et al., 1996)

(vp), the relative importance of these dynamic processes differs. The collision theory classifies three regimes according to the value of the parameter defined as K, defined as:

$$K = \frac{Z_p}{Z_T} \times \frac{V_e}{V_p} \tag{1.1}$$

Where:

- V_e is the velocity of the electron in an atomic (or molecular) target layer,
- V_p is the velocity of the incident ion (projectile) ,
- Z_p and Z_T are the atomic numbers (charges) of the projectile and the target, respectively.

Three regimes are distinguished:

1.2.1 Low-impact velocity regime (K » 1):

This regime, also called the strong interaction regime, is reached when the collision velocity (Vp) is much lower than that of the active electron (Ve). The theory adapted to this regime is based on the hypothesis of the formation of a transient quasi-molecule during the collision and relies on representing electronic states using molecular bases. One of its models is **C**ontinuum **D**istorted **W**ave (CDW) model, where the target continuum wave is distorted by the projectile wave.

1.2.2 High-velocity impact regime (K « 1)

This regime, also called the perturbative regime, is reached at high collision velocities (Vp » Ve) and for large asymmetries (Zp « ZT). A first-order perturbation theory, such as the **P**lane **W**ave **B**orn **A**approximation (PWBA), becomes reliable for accurately evaluating the total cross-sections of ionization and excitation reactions.

1.2.3 Intermediate impact velocity regime ($K \approx 1$)

Quasi-symmetric regime, where we observe:

- Strong coupling between capture and excitation channels.
- Cross-sections of different atomic processes are close to their maximum values.
- Multiple processes have non-negligible probabilities.

The ionization process becomes increasingly significant as the impact velocity increases. This process is mainly due to electrons ejected with low kinetic moments around the target and the projectile. Electron capture is the dominant process in the low-velocity collision regime. In contrast, ionization and excitation prevail at high collision velocities.

1.3 Main theoretical methods developed:

Determining the wave function that depicts the scattering wave is the most important aspect of a collision problem since it includes all of the information on the system's state. Over the past decades, a number of approximations have been used to address the problem.

We will now briefly present the main theoretical approaches that have been used so far to study the excitation processes in light systems.

1.3.1 Born Approximation:

Initially, it should be noted that the Born approximation is essentially a perturbative expansion of the wave function or the scattering amplitude in powers of the interaction potential.

In this approach we start with the time-independent Schrödinger equation to derive the integral equations of the wave function. We must then consider the appropriate boundary conditions related to large distances. That is, a specific choice of the Green's function and the homogeneous solution of the differential equation determines the definition of the boundary conditions. The same result can also be obtained by using the time-dependent Schrödinger equation and Green's function. [34]

In an atom-ion collision, the transition of an electron is considered from the initial state $|a\rangle$ in the entrance channel to the final state $|b\rangle$ in the exit channel.
In this perturbation treatment, the matrix element of transition $T_{\beta\alpha}$ .can be expresses as:

$$T_{\beta\alpha} = \langle\beta|V_\beta|\psi_a^+\rangle \tag{1.2}$$

Where $|\Psi_\alpha^+\rangle$ represents the eigenvector of the total Hamiltonian H in the exit channel and satisfies the Lippmann-Schwinger equation:

$$|\psi_a^+\rangle = |\alpha\rangle + G^+V_\alpha|\alpha\rangle \tag{1.3}$$

Where:

$$G^+ = \lim_{\epsilon\to 0}(E - H + i\epsilon)^{-1} \tag{1.4}$$

is the Green operator, where E is the total energy of the system, and H is the total Hamiltonian of the system. This Hamiltonian can be written as:

$$H = H_\alpha + V_\alpha = H_\beta + V_\beta \tag{1.5}$$

$|\alpha\rangle, H_\alpha, V_\alpha$

are respectively the eigenvector, the Hamiltonian of the particles without interaction, and the interaction potential in the input channel.

$|\beta\rangle, H_\beta, V_\beta$ are respectively the eigenvector, the Hamiltonian of the particles without interaction, and the interaction potential in the output channel.

Using the general identity relating the inverses of two operators and with the help of equation (I-5), we can write G^+ in the form:

$$G^+ = G^+_\alpha + G^+_\alpha V_\alpha G^+ \tag{1.6}$$

Where

$$G^+_\alpha = \lim_{\epsilon \to 0} (E - H_\alpha + i\epsilon)^{-1} \tag{1.7}$$

From equation (I-6), we can easily derive the following series:

$$G^+ = G^+_\alpha \sum_{n=0}^{+\infty} (V_\alpha G^+_\alpha)^n \tag{1.8}$$

By substituting the expression G^+ into equation (I-3), we obtain:

$$T_{\beta\alpha} = \langle\beta|V_\beta \left[1 + G^+_\alpha \sum_{n=0}^{+\infty} (V_\alpha G^+_\alpha)^n V_\alpha\right] |\alpha\rangle \tag{1.9}$$

Thus, by retaining only the first term, we obtain the first-order Born approximation (Born-I):

$$T^{B1}_{\beta\alpha} = \langle\beta|V_\beta|\alpha\rangle \tag{1.10}$$

The first-order Born approximation is only valid for atomic collisions with high-energy ions. Similarly, the second-order Born approximation consists of retaining only the first two terms of series (I-9):

$$T^{BII}_{\beta\alpha} = \langle\beta|V_\beta + V_\beta G^+_\alpha V_\alpha|\alpha\rangle \tag{1.11}$$

And so on, the N^{th} order of the Born approximation consists of retaining only the first N terms of the series.

The Born approximation is only valid and provides good results when the kinetic energy of the incident ion is very high compared to the interaction potential.

1.3.2 VPS Approximation (Vainshtein, Presnyakov, and Sobelman):

A new approach was developed in the early 1960s by Vainshtein, Presnyakov, and Sobelman, known as the "VPS approximation," to address the distortions of the outgoing wave function describing the collisional system.

This method considers the interaction between the projectile and the active electron, as well as between the projectile and the target nucleus, to ensure compatibility with the conditions of the collision process. McCarroll and Crothers proposed a slightly different version of the initial approach, which was applied in 1966 by McCarroll and Salin to proton-hydrogen collisions.

1.3.3 Coupled-Channels Approximation (Close-Coupling):

Another alternative to the Born approximation is the coupled-channel approximation, where the scattering wave function is expanded in terms of a basis of wave functions representing the different reaction channels. This leads to a system of coupled differential equations for the expansion coefficients. [34] We assume that the projectile follows a straight-line trajectory and is perpendicular to the momentum transfer of the target, according to the following equations:

$$\vec{R} = \vec{\rho} + z \tag{1.12}$$

$$\dot{z} = vt \tag{1.13}$$

$$\vec{\rho} \cdot \vec{v} = 0 \tag{1.14}$$

Where:

- $\vec{R}$ is the projectile-target distance.
- $\vec{V}$ is the projectile's incident velocity.
- $\vec{\rho}$ is the impact parameter.
- t Is the time arbitrarily set to zero when $\vec{R} = \vec{\rho}$.

The Schrödinger equation can be written as

$$\left\{ -iv\frac{\partial}{\partial z} + H(z) + V(\vec{R}(z)) \right\} \left| \psi^{+}(\vec{\rho}, \vec{z}) \right\rangle = 0 \tag{1.15}$$

where H is the electronic Hamiltonian of the system without interaction potential, which is responsible for the electronic transition. The wave function can be approximated by expanding it over a truncated basis of eigenstates $\{|\chi_i\rangle\}$, which are the eigenvectors of H. We assume:

$$\left|\psi^+(\vec{\rho},\vec{z})\right\rangle = \sum_{k=1}^{n} a_k(\vec{\rho},\vec{z})|\chi_k\rangle \exp\left(-i\epsilon_k z/v\right) \tag{1.16}$$

where ϵ_k represents the eigenenergy of the eigenstate χ_k.

By substituting the above expression for $|\psi^+(\vec{\rho},\vec{z})\rangle$ into equation (1-13), we obtain a system of coupled differential equations for the functions $a_j(\vec{\rho},\vec{z})$, after projection onto $\langle\chi_j|$:

$$i\frac{\partial}{\partial z}\, a_j(\vec{\rho},\vec{z}) = \sum_{k=1}^{n} V_{jk}\big(\vec{R}(z)\big)\ \exp\Big(i\,(\epsilon_j-\epsilon_k)\frac{z}{v}\Big)\, a_k(\vec{\rho},\vec{z}) \tag{1.17}$$

where the matrix elements $V_{jk}\big(z\big)$ are given by:

$$V_{jk}\big(\vec{R}(z)\big) = \langle\chi_j|\, V\big(\vec{R}(z)\big)\, |\chi_k\rangle \tag{1-16}$$

With the asymptotic conditions:

$$a_j(\vec{\rho}, z(t\to-\infty)) = \delta_{ji} \tag{1-17}$$

The index i corresponds to the initial state of the system in the entrance channel.

$$a_j(\vec{\rho},t) = \int_{-\infty}^{t} dt \sum_{k=1}^{n} V_{jk}\big(\vec{R}(t)\big)\exp\big(i(\epsilon_j-\epsilon_k)t\big)a_k(\vec{\rho},t) \tag{1.18}$$

The probability of transition into a particular reaction channel f is given by the coefficient of the wave function expansion in this channel. It is therefore

$$P = \left|a_f\left(\vec{\rho},+\infty\right)\right|^2 \tag{1.19}$$

We will now briefly present the different choices of basis that have been made, which depend both on the velocity and the asymmetry of the collision:

- **Single-Centered Expansion (SCE):** The scattering wave function is expanded using a basis of atomic states, which are the eigenvectors of the target Hamiltonian. This basis is referred to as "single-centered," meaning it is centered on the target.

- **Two-Centered Atomic Orbital (TCAO):** In the low-velocity regime, the capture cross-sections become large. As a result, capture channels that involve projectile states are open, and the wave function cannot be expanded solely using the target states. During excitation through transitions via intermediate states centered on the projectile (and thus through capture channels), the traditionally used method consists of expanding $|\psi^+(\vec{\rho},\vec{z})\rangle$ using a so-called "two-centered" basis. [1]

$$\left|\psi^+(\vec{\rho},\vec{z})\right\rangle = \sum_{k=1}^{n} a_k\left(\vec{\rho},\vec{z}\right)|\chi_k^c\rangle \exp\left(-i\,\epsilon_k\,\frac{z}{v}\right) + \sum_{j=1}^{m} b_j\left(\vec{\rho},\vec{z}\right)|\chi_l^p\rangle \exp\left(-i\,\epsilon_l\,\frac{z}{v}\right) \qquad (1.20)$$

$|\chi_k^c\rangle$ and $|\chi_l^p\rangle$ are, respectively, the eigenstates of the target and the projectile.

- **One-and-a-Half Centered Expansion (OHCE):** In this method, the ionization of the target due to capture by the projectile is represented by including a few functions centered on the projectile in the expansion of the scattering wave function over the target orbitals

1.3.4 Glauber Approximation:

This approach was developed by Glauber in the late 1950s. It is one of the formulations of the eikonal approximation. It also allows for the introduction of interaction potential effects in the wave function describing the final state of the system. The eikonal approximation assumes that the projectile moves in a straight line and the momentum transfer of the target is perpendicular to the projectile's trajectory.

The influence of the interaction potential on the scattering wave function is manifested by a deformation of the plane wave representing the projectile when it approaches or moves away from the target.

1.3.5 Variational approach:

Several methods have been developed to provide models suitable for studying the collision process. We cite the Cheshire model, established in 1968 [48], in which the author developed the interaction and function of onde on spherical harmonics; the Bransden and Coleman model of second-order potential, proposed in 1972 [8] and based on the method of coupled routes; and the model of pseudo-states, first used by Reading et al. in 1976 [12], then again by Fichard et al. [16], and finally by Swafford et al 1977 [61].the model of Scheshire and Sullivan [12] in which these authors developed the interaction and the wave function on a set of spherical harmonics.

The majority of the approaches described so far, primarily concerning the study of high-energy collisions (with the exception of the coupled equations method, whose application can be extended to the medium energy domain), have revealed their limitations in accounting for coupling effects either because calculations become very complex with the inclusion of continuum states or because the approaches themselves are inaccurate.

Another alternative emerged with the development of a new approach:

the variational principle of Schwinger, which was introduced by Schwinger in 1950 to remedy these shortcomings.It constitutes a powerful and effective tool for studying the proton-hydrogen atom collision or, more generally, for studying the collision of multicharged ions with atoms at intermediate speeds.

In 1979, Luchessse and McKoy [41] applied the Schwinger variational principle to the electronic diffusion, in which the main object is to show that the Schwinger variational approach gives excellent solutions to the diffusion problems without requiring some developments on important basis. Thereafter, Lucchese, Watson, and V. McKoy [42] developed this approach in the case of the elastic diffusion of electrons by molecules; indeed, their objective was to show that the amplitude of diffusion deducted from this variational principle converges quickly in relation to the basis on which the diffusion wave function is developed.

To investigate the electronic excitation of atoms by ion collisions, a variational method based on the Schwinger variational principle was presented years ago. This approach that has been implemented within the impact parameter framework successfully predicted the saturation of the excitation of ions by neutral projectiles at intermediate impact velocities(B. Brendlé et al. 1985 [10],K. Wohrer et al. 1986 [66],M. Bouamoud 1988 [7],R. Gayet and M. Bouamoud 1989 [18],B. Lasri 1998 [33],B. Lasri, M. Bouamoud and R. gayet 2004 [35],B. Lasri, A Bouserhane, M. Bouamoud et R. Gayet (2005) [38] ,B. Lasri, M. Bouamoud et R. Gayet (2006) [36], B. Lasri, M. Bouamoud et J. Hanssen [37])

Chapter 2

Schwinger Variational Approach for collision Theory

2.1 Introduction:

Variational approaches have demonstrated their efficacy during the last few decades as a crucial investigative tool in theoretical physics, especially for the investigation of atomic collision processes, and in chemistry, for instance, in resolving the bound state issue. These variational methods can be divided into two groups for collision problems: those based on the Lippmann-Schwinger equation (the variational method, which Schwinger himself presented in his lectures at Harvard University and was published in 1947) [26] and those based on the Schrödinger equation (the Hulthén-Khon method [24,30], the so-called **R-matrix** variational method) [55, 57].

One of the most interesting approaches is the one proposed by J. Schwinger, hence the name "Schwinger variational principle," for calculating the scattering amplitude. It is thus based on the Lippmann-Schwinger integral equations.

The variational principle of Schwinger consists of obtaining a stationary form of the transition amplitude with respect to small variations of the scattering states.

In this chapter, the stationary expressions of the transition amplitude in the case of a collision have been presented.

2.2 Stationary Forms of the Transition Amplitude:

During a collision between two particles, the scattering states $|\psi_\alpha^+\rangle$ and $|\psi_\beta^-\rangle$, which are eigenvectors of the total Hamiltonian of the system, satisfy the incoming and outgoing wave conditions, respectively. These states are defined, in the case of a collision without rearrangement, by the Lippmann-Schwinger equations:

$$|\psi_\alpha^+\rangle = |\alpha\rangle + G_c^+|\psi_\alpha^+\rangle \tag{2.1a}$$

$$|\psi_\beta^-\rangle = |\beta\rangle + G_c^- V_c|\psi_\beta^-\rangle \tag{2.1b}$$

$|\alpha\rangle$ and $|\beta\rangle$ respectively denote the initial and final states of the target, and G_c^+ is the Green's operator defined by:

$$G_c^+ = (E - H_c + i\epsilon)^{-1} \tag{2.1c}$$

E is the total energy of the system.

If we denote by H_c the Hamiltonian of the non-interacting particles and by V_c the interaction potential in channel C , the total Hamiltonian of the system can be written as:

$$H = H_c + V_c \tag{2.2}$$

The transition amplitude, defined as the transition matrix element, is written as:

$$T_{\beta\alpha} = \langle\beta|T|\alpha\rangle \tag{2.3}$$

Furthermore, from the Lippmann-Schwinger equations (2.1a,b), it can also be deduced that the transition amplitude given by the previous relation can be written in three forms:

$$T_{\beta\alpha} = \langle\beta|V_c|\psi_a^+\rangle \tag{2.4a}$$

$$= \langle\psi_\beta^-|V_c|\alpha\rangle \tag{2.4b}$$

$$= \langle\psi_\beta^-|V_c - V_c G_c^+ V_c|\psi_a^+\rangle \tag{2.4c}$$

It can be easily observed that, from a simple combination of the previous expressions (2.4a-c), a new form $T_{\beta\alpha}$ called the bilinear form of Schwinger's variational principle [56], is written as:

$$T_{\beta\alpha} = \langle\beta| V_C \left|\psi_\alpha^+\right\rangle + \left\langle\psi_\beta^-\right| V_C |\alpha\rangle - \left\langle\psi_\beta^-\right| V_C - V_C G_C^+ V_C \left|\psi_\alpha^+\right\rangle \tag{2.5}$$

This last expression is stationary with respect to small arbitrary variations $|\delta\psi_\alpha^+\rangle$ and $\left\langle\delta\psi_\beta^-\right|$ of the vectors$|\psi_\alpha^+\rangle$ and $\left\langle\psi_\beta^-\right|$ around their exact values.

Indeed, by differentiating relation (2.5), we obtain:

$$\delta T_{\beta\alpha} = \left[\langle\beta| - \left\langle\psi_\beta^-\right| + \left\langle\psi_\beta^-\right| V_C G_C^+\right] V_C \left|\delta\psi_\alpha^+\right\rangle + \left\langle\delta\psi_\beta^-\right| V_C \left[|\alpha\rangle - \left|\psi_\alpha^+\right\rangle + G_C^+ V_C \left|\psi_\alpha^+\right\rangle\right] \tag{2.6}$$

Knowing that $|\psi_\alpha^+\rangle$ and $\langle\psi_\beta^-|$ satisfying the Lippmann-Schwinger integral equations (2.1a,b), relation (2.6) indeed gives:

$$\delta T_{\beta\alpha} = 0 \tag{2.7}$$

Thus, we will say that the error made $T_{\beta\alpha}$ is quadratic with respect to the one made on the scattering states.

Note that equations (2.4a-c) are exact expressions for the transition amplitude. This means that an exact amplitude is obtained when the exact scattering states $|\psi_\alpha^+\rangle$ and $\langle\psi_\beta^-|$ are used.

Following the same procedure mentioned above and using equations (2.4a-c),

We can obtain a new stationary representation of the transition amplitude $T_{\beta\alpha}$ in the fractional form of Schwinger's variational principle:

$$T_{\beta\alpha} = \frac{\langle\beta| V_C |\psi_\alpha^+\rangle \left\langle\psi_\beta^-\right| V_C |\alpha\rangle}{\left\langle\psi_\beta^-\right| V_C - V_C G_C^+ V_C |\psi_\alpha^+\rangle} \tag{2.8}$$

Taking into account the equivalent expressions (2.4a-c) for the transition amplitude during the differentiation of this expression, it can always be verified that

$$\delta\Gamma_{\beta\alpha} = \left[\langle\beta| - \left\langle\psi_\beta^-\right| + \left\langle\psi_\beta^-\right| V_C G_C^+\right] V_C \left|\delta\psi_\alpha^+\right\rangle + \left\langle\delta\psi_\beta^-\right| V_C \left[|\alpha\rangle - \left|\psi_\alpha^+\right\rangle + G_C^+ V_C \left|\psi_\alpha^+\right\rangle\right] = 0 \tag{2.9}$$

is identical to expression (2.6), which means that it $T_{\beta\alpha}$ is also stationary with respect to small arbitrary variations of the scattering states $|\psi_\alpha^+\rangle$ and $\left\langle\psi_\beta^-\right|$ around their exact values.

Moreover, this fractional form has the advantage of being independent of the normalization chosen for the scattering states. It is important to recall that this variational principle, like the bilinear form given by equations (2.5), automatically introduces the correct boundary conditions (i.e., it does not require trial wave functions to satisfy the boundary conditions as in the Hulthén-Kohn method [24]) and only uses trial wave functions in the region where the interaction occurs. As a first illustration, the Born approximation (Born-I) consists in replacing, respectively in expression (2.8), the unknown exact vectors $|\psi_\alpha^+\rangle$ and $\left\langle\psi_\beta^-\right|$ with the trial vectors $|\alpha\rangle$ and $\langle\beta|$, that is:

$$\left|\psi_\alpha^+\right\rangle = |\alpha\rangle \tag{2.10a}$$

and

$$\left\langle\psi_\beta^-\right| = \langle\beta| \tag{2-10b}$$

With this simple choice of trial functions, the fractional expression of the transition amplitude becomes:

$$T_{\beta\alpha} = \frac{\langle\beta|V_C|\alpha\rangle\langle\beta|V_C|\alpha\rangle}{\langle\beta|V_C - V_C G_C^+ V_C|\alpha\rangle} \tag{2.11}$$

under another formulation:

$$T_{\beta\alpha} = T^{BI}\left[\frac{1}{1-\frac{\bar{T}^{BII}}{T^{BI}}}\right] \tag{2.12}$$

such as:

T^{BI} corresponds to the first-order Born approximation for the transition amplitude. The second-order Born approximation for the transition amplitude, denoted T^{BII}, is such that:

$$T^{\mathrm{BII}} = T^{\mathrm{Bl}} + \bar{T}^{\mathrm{BII}} \tag{2.13}$$

We can emphasize that in the case where the ratio $\left|\frac{\bar{T}^{\mathrm{BII}}}{T^{\mathrm{BI}}}\right|$ is small compared to 1, and using the expansion of expression (2.12)($(1-\varepsilon)^{-1} \cong (1+\varepsilon) \quad \varepsilon < 1$), we obtain:

$$T_{\beta\alpha} = T^{\mathrm{BI}} + \bar{T}^{\mathrm{BII}} + \ldots\ldots.. \tag{2.14}$$

We observe that in this expansion, the first two terms correspond to the 2$^{\mathrm{nd}}$-order Born approximation.

Consequently, we can conclude that in the case of sufficiently high energies for which the Born series converges, the Schwinger variational principle could provide a better approximation than the 2^{nd}-order Born approximation.

An evaluation of the transition amplitude in its fractional form, given by equation (2.8), and the use of approximation (2.10 a,b) with more complex choices have been carried out for $^3S_1$ in a nucleon-nucleon collision described by a Yukawa potential [24] or a Gaussian potential [56]. The variational result is indeed more accurate than the 2^{nd}-order Born approximation. However, this statement is meaningless at low energy, where the Born series does not converge.

In fact, the first Born approximation gives cross sections that are less accurate than the variational estimate based on a simple choice (2.10a,b). Such an example illustrates the difficulties that can arise when a poor choice of trial functions is used in the variational principle. The application of the variational expression (2.12) to weaker interactions provides more satisfactory results [56].

2.3 Approximated variational amplitude in the Schwinger formalism

As the scattering states $|\psi_\alpha^+\rangle$ and $\langle\psi_\beta^-|$ cannot be known exactly, we take as trial states the vectors $\left|\widetilde{\psi}_\alpha^+\right\rangle$ and $\left\langle\widetilde{\psi}_\beta^-\right|$, such that:

$$\left|\widetilde{\psi}_\alpha^+\right\rangle = |\psi_\alpha^+\rangle + |\delta\psi_\alpha^+\rangle \tag{2.15a}$$

and

$$\left\langle\tilde{\psi}_\beta^-\right| = \langle\psi_\beta^-| + \langle\delta\psi_\beta^-| \tag{2.15b}$$

Expanding $\left|\tilde{\psi}_\alpha^+\right\rangle$ and $\left\langle\tilde{\psi}_\beta^-\right|$ in terms of the states of a truncated basis $\{|i\rangle\}$ and $\{\langle j|\}$, respectively (these two sets are not necessarily identical, but they have the same finite dimension N):

$$\left|\tilde{\psi}_\alpha^+\right\rangle = \sum_{i=1}^{N} \tilde{a}_i |i\rangle \tag{2.16a}$$

$$\left\langle\tilde{\psi}_\beta^-\right| = \sum_{j=1}^{N} \tilde{b}_j^* \langle j| \tag{2.16b}$$

The coefficients $\tilde{a}_i$ and $\tilde{b}_j$, which are components of the approximated scattering states, are determined by solving the equation $\delta T_{\beta\alpha} = 0$.

Substituting these trial states into expression (2.8), we obtain the approximated transition amplitude $\widetilde{T}_{\beta\alpha}$:

$$\tilde{T}_{\beta\alpha} = \frac{\langle\beta|V_C \left|\tilde{\psi}_\alpha^+\right\rangle \left\langle\tilde{\psi}_\beta^-\right| V_C|\alpha\rangle}{\left\langle\tilde{\psi}_\beta^-\right| V_C - V_C G_C^+ V_C \left|\tilde{\psi}_\alpha^+\right\rangle} \tag{2.17}$$

From equations (2.6) and (2.15a,b), we derive the following equation:

$$\delta T_{\beta\alpha} = \left[\langle\beta| - \left\langle\widetilde{\psi}_\beta^- - \delta\psi_\beta^- \left(1 - V_C G_C^+\right)\right] V_C \left|\delta\psi_\alpha^+\right\rangle + \left\langle\delta\psi_\beta^-\right| V_C||\alpha\right\rangle - \left(1 - G_C^+ V_C\right)\left|\widetilde{\psi}_\alpha^+ - \delta\psi_\alpha^+\right\rangle\right] \tag{2.18}$$

It is easy to show that for any first-order variation in $|\delta\psi_\alpha^+\rangle$ and $\left\langle\delta\psi_\beta^-\right|$, we have $\delta T_{\beta\alpha} = 0$.

Now, using the equation $\delta\Gamma_{\beta\alpha} = 0$ and replacing the vectors $\left|\widetilde{\psi}_\alpha^+\right\rangle$ and $\left\langle\widetilde{\Psi}_\beta^-\right|$ by their previous expansions in equations (2.16a,b), we obtain the following two coupled equations for the coefficients $\tilde{a}_i$ and $\tilde{b}_j$:

$$\begin{cases} \langle j|V_C|\alpha\rangle - \sum_{i=1}^{N} \tilde{a}_{i\alpha} \langle \mathrm{j}|V_C - V_C G_C^+ V_C|i\rangle = 0 \\ \langle\beta|V_C|i\rangle - \sum_{j=1}^{N} \tilde{b}_j^* \langle \mathrm{j}|V_C - V_C G_C^+ V_C|i\rangle = 0 \end{cases} \tag{2.19}$$

Let D be the square matrix of dimension N whose elements are:

$$D_{ji} = \langle j|V_C - V_C G_C^+ V_C|i\rangle \tag{2.20}$$

and let V_α and V_β be column vectors with elements:

$$\langle V_\alpha\rangle_j = \langle j|V_C|\alpha\rangle \tag{2.21a}$$

$$|V_\beta|_i = \langle i|V_C|\beta\rangle \tag{2.21b}$$

Defining $\tilde{a}$ and $\tilde{b}$ as column vectors with elements $\tilde{a}_i$ and $\tilde{b}_j$, the coupled equations in system (2.19) can be written in matrix form as:

$$V_\alpha = D \cdot \tilde{a} \tag{2.22a}$$

$$\left(V_\beta^*\right)^t = \tilde{b}^* \cdot D \tag{2.22b}$$

or, using matrix algebra properties:

$$\tilde{a} = D^{-1} \cdot V_\alpha \tag{2.23a}$$

$$\tilde{b}^* = \left(V_\beta^*\right)^t \cdot D^{-1} \tag{2.23b}$$

These equations provide solutions for the components $\tilde{a}_i$ and $\tilde{b}_j$ of the trial states $\left|\widetilde{\psi}_\alpha^+\right\rangle$ and $\left\langle\widetilde{\psi}_\beta^-\right|$.

Finally, substituting these trial states into expression (2.17) for the approximated transition amplitude $\widetilde{T}_{\beta\alpha}$, we obtain:

$$\tilde{T}_{\beta\alpha} = \sum_{i=1}^{N}\sum_{j=1}^{N} \langle\beta|V_C|i\rangle \left(D^{-1}\right)_{ij} \langle j|V_C|\alpha\rangle \tag{2.28}$$

where $D_{ji} = \langle j|V - VG_T^+V|i\rangle$, and $\left(D^{-1}\right)_{ij}$ is the matrix element of D^{-1}, the inverse of matrix D relative to the basis vectors $|i\rangle$ and $|j\rangle$.

In conclusion, we have determined the approximated transition amplitude $\widetilde{T}_{\beta\alpha}$ in terms of the approximated scattering states, which have been expanded in a finite-dimensional vector subspace of size N.

Chapter 3

Schwinger Variational Treatment for the Atomic Excitation of Ions

3.1 Introduction

Understanding the mechanisms of atomic collisions by ion impact constitutes the main interest of researchers for testing the theoretical methods and models designed to study and test these collision processes. This will require a reliable theory that adequately describes the interaction of the nuclei with the electrons via the Coulomb force because of its long range. Even for the simplest cases,this collision problem cannot be solved. For this reason, the theory of ion-atom collision has concentrated on developing techniques, methods, and approximations in which various types of ion-atom collisions can be described. The excitation process in ion-atom collisions has received considerable interest over the past decades (Gayet and Hanssen, 1992, 1994 [19] [20]. However, in recent years, as demonstrated by R. Gayet and B. Brendlé (1985) [10], R. Gayet and M. Bouamoud (1988, 1989) [7] [18], and B. Lasri et al. (1998, 2004) [33] [35], new techniques have been developed based on the fractionele vorm van Schwingers variatieprincipe. The computed cross-sections show excellent agreement with available experimental data.

3.2 Schwinger Variational Amplitude for Direct Excitation

In the formalism of the impact parameter, specially adapted to direct excitation, the calculation of the variational transition amplitude was previously described by M. Bouamoud (1988) [7], R. Gayet and M. Bouamoud (1989) [18], B. Lasri (1998) [33], and B. Lasri, M. Bouamoud, and R. Gayet (1998) [35]. Thus, our primary objective in this section is to apply Schwinger's variational principle to the excitation of a hydrogenoid system by ion impact at intermediate speeds.

Since the main contribution to the considered transition occurs at small angles (for example, $< 10^{-3}$ for a $H^+ \rightarrow H$ type collision at an energy of 50 keV), the projectile can be assumed to follow a straight-line trajectory. Therefore, this problem can be treated within the framework of the eikonal approximation. [28] The eikonal method is a semi-classical approach that assumes the nuclei move in a classical manner, while the motion of the electrons is treated quantum mechanically.

For this, let us consider a collision between a projectile of mass M_P and charge Z_P and a target of mass M_T and chargeZ_T. In the impact parameter method based on the description of the relative motion of the nuclei following a classical straight-line trajectory, the internuclear separation is given by:

$$\vec{R} = \vec{\rho} + \vec{z} \tag{3.1a}$$

$$\vec{z} = \vec{v}.t \tag{3.1b}$$

$$\vec{\rho} \cdot \vec{v} = 0 \tag{3.1c}$$

Where:

$\vec{R}$ is the internuclear distance.

$\vec{\rho}$ is the impact parameter.

$\overrightarrow{\mathrm{v}}$ is the relative velocity of the projectile.

t is the time, arbitrarily set to zero when $\vec{R} = \vec{\rho}$.

The geometry of the system is described by the following figure, 3-1.

With:

- $\vec{X}$ as the position of the electron relative to the target T.

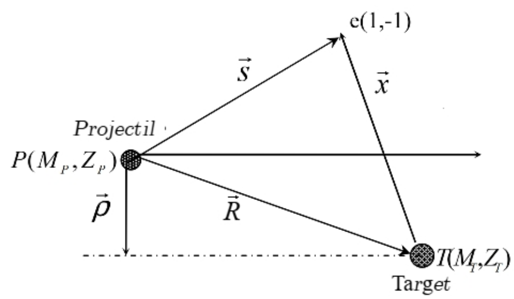

Figure 3.1: Collisional System

- $\vec{s}$ as the position of the electron relative to the projectile P.

By adopting a center-of-mass frame for the projectile-target system, the total Hamiltonian of the system in the case of a single rearrangement channel c is given by:

$$H = H_C + V_C \tag{3.2}$$

H_C is the Hamiltonian of the non-interacting particles, given by $H_C = H_T + T_P$, with:

$$H_T = \frac{\Delta_x}{2} - \frac{Z_T}{x} \tag{3.3a}$$

and

$$T_P = \frac{1}{2\mu}\Delta_R \tag{3.3b}$$

where μ represents the reduced mass, given by:

$$\mu = \frac{M_P\,(M_T + 1)}{M_P + M_T + 1} \tag{3.4}$$

V_C is the interaction potential between the colliding particles. This potential is expressed as:

$$V_C = \frac{Z_P Z_T}{R} - \frac{Z_P}{S} \tag{3.5}$$

The inter-cluster potential V_{int} is defined by the long-range Coulomb interaction between the projectile and the target, namely:

$$V_{\text{int}} = \frac{Z_P\left(Z_T-1\right)}{R} \tag{3.6}$$

where Z_P and Z_T represent the charge of the projectile and the charge of the target, respectively. In 1972, R. K. Janev and A. Salin [27], and later in 1979, D. Z. Belkic, R. Gayet, and A. Salin [5], demonstrated that the total cross-sections are independent of the inter-cluster potential V_{int} given by equation (3.6).

In the calculation of the transition amplitude, the influence of this potential is reduced to a phase factor dependent on the impact parameter $\vec{\rho}$, given by: $\rho^{\frac{2iZ_P\left(Z_T-1\right)}{\mathrm{v}}}$.

However, its contribution to the differential cross-section must be reintroduced. This leads us to neglect the influence of the inter-cluster potential when calculating the transition amplitude, and thus define the interaction responsible for the excitation as:

$$V = V_C - \frac{Z_P\left(Z_T-1\right)}{R} \tag{3.7a}$$

$$= Z_P\left(\frac{1}{R}-\frac{1}{S}\right) \tag{3.7b}$$

Dans une collision sans réarrangement, et selon le formalisme du paramètre d'impact, les états de diffusion $\left|\psi_\alpha^+(z)\right\rangle$ et $\left|\psi_\beta^-(z)\right\rangle$, vecteurs propres de l'hamiltonien total du système, satisfaisant respectivement aux conditions d'onde sortante et entrante, sont définis grâce aux équations de Lippmann-Schwinger iconales [28]:

$$\left|\psi_\alpha^+(z)\right\rangle = |\alpha(z)\rangle + \int_{-\infty}^{+\infty} dz' G_T^+\left(z-z'\right) V\left(z'\right)\left|\psi_\alpha^+\left(z'\right)\right\rangle \tag{3.8a}$$

$$\left|\psi_\beta^-(z)\right\rangle = |\beta(z)\rangle + \int_{-\infty}^{+\infty} dz' G_T^-\left(z-z'\right) V\left(z'\right)\left|\psi_\beta^-\left(z'\right)\right\rangle \tag{3.8b}$$

where V is the interaction potential between the projectile and the target. $|\alpha(z)\rangle$ and $|\beta(z)\rangle$ are the initial and final states of the target, respectively.

These scattering states are solutions of the Schrödinger equation in the impact parameter method, namely:

$$\left\{-i\mathrm{v}\frac{\partial}{\partial z}+H_T(z)+V\right\}\left|\psi_\alpha^+(z)\right\rangle=0 \tag{3.9a}$$

$$\left\{-i\mathrm{v}\frac{\partial}{\partial z}+H_T(z)+V\right\}\left|\psi_\beta^-(z)\right\rangle=0 \tag{3.9b}$$

It should be noted that the notations $|\psi_\alpha^+(z)\rangle$, $\left|\psi_\beta^-(z)\right\rangle$, $|\alpha(z)\rangle$ and $|\beta(z)\rangle$ mean that the scattering states $|\psi_\alpha^+\rangle$ and $\left|\psi_\beta^-\right\rangle$ as well as $|\alpha\rangle$ and $|\beta\rangle$ do not depend only on the electronic coordinates $\vec{x}$ but also on the z component of $\vec{R}$. The states $|\alpha(z)\rangle$ and $|\beta(z)\rangle$, which represent the initial and final states of the target, respectively, are solutions of the eikonal Schrödinger equation with only the target Hamiltonian H_T:

$$\left\{-iv\frac{\partial}{\partial z}+H_T(z)\right\}|\alpha(z)\rangle=0 \tag{3.10a}$$

$$\left\{-iv\frac{\partial}{\partial z}+H_T(z)\right\}|\beta(z)\rangle=0 \tag{3.10b}$$

By considering a configuration space where the origin of the coordinates is at the nucleus of the target, we obtain:

$$\alpha(z)=\langle\vec{x},z\mid\alpha(z)\rangle=e^{-i\frac{\varepsilon_\alpha}{\mathrm{v}}z}\phi_\alpha(\vec{x}) \tag{3.11a}$$

$$\beta(z)=\langle\vec{x},z\mid\beta(z)\rangle=e^{-i\frac{\varepsilon}{\mathrm{v}}z}\phi_\beta(\vec{x}) \tag{3.11b}$$

where ε_α and ε_β represent the eigenenergies of the states ϕ_α and ϕ_β, respectively. $\vec{x}$ is the distance separating the nucleus and the electron, i.e., the set of electronic coordinates.

The Green's functions $G_T^\dagger(z-z')$ and $G_T^-(z-z')$ correspond to the eikonal Green's function $G_C^\pm$ associated with the Hamiltonian H_C . $G_T^\dagger(z-z')$ satisfies the following equation:

$$\left(-iv\frac{\partial}{\partial z}+H_T\right)G_T^+(z-z')=-\delta(z-z') \tag{3.12}$$

with the initial conditions:

$$\begin{aligned} G_T^{+}(z) &= 0 \quad z < 0 \\ G_T^{-}(z) &= 0 \quad z > 0 \end{aligned} \tag{3.13b}$$

By solving equation (3.12), we can directly and generally show that we have:

$$G_T^{\pm}\left(z-z'\right)\left|\nu\left(z'\right)\right\rangle = -\frac{i}{\mathrm{v}}|\nu(z)\rangle\theta\left(z-z'\right) \quad (\nu=\alpha,\beta) \tag{3.14}$$

where $\theta\left(z-z'\right)$ is the Heaviside function. and which gives for $|\alpha(z)\rangle$:

$$G_T^{+}\left(z-z'\right)\left|\alpha\left(z'\right)\right\rangle = \begin{cases} \frac{i}{\mathrm{v}}|\alpha(z)\rangle & \mathrm{z}>\mathrm{z}' \\ 0 & \mathrm{z}<\mathrm{z}' \end{cases} \tag{3.15a}$$

Similarly, for $|\beta(z)\rangle$, we find:

$$G_T^{+}\left(z-z'\right)\left|\beta\left(z'\right)\right\rangle = \begin{cases} -\frac{i}{\mathrm{v}}|\beta(\mathrm{z})\rangle & \mathrm{z}>\mathrm{z}' \\ 0 & \mathrm{z}<\mathrm{z}' \end{cases} \tag{3.15b}$$

Now, if we denote by the notation [|] the integration over electronic coordinates, we can show that the transition amplitude is written as:

$$a_{\beta\alpha}(\vec{\rho}) = \lim_{z\to+\infty}\left\lfloor\beta(z)\mid\psi_\alpha^{+}(z)\right\rfloor = \lim_{z\to+\infty}\left\lfloor\psi_\beta^{-}(z)\mid\alpha(z)\right\rfloor \tag{3.16}$$

That is:

$$a_{\beta\alpha}(\vec{\rho}) = \delta_{\beta\alpha} + \lim_{z\to+\infty}\int_{-\infty}^{z} d\left[\beta(z)\mid\psi_\alpha^{+}(z)\right] \tag{3.17a}$$

or

$$a_{\beta\alpha}(\vec{\rho}) = \delta_{\beta\alpha} + \lim_{z\to+\infty}\int_{-\infty}^{z}\frac{dz}{dz}d\left[\beta(z)\mid\psi_\alpha^{+}(z)\right] \tag{3.17b}$$

From equations (3.9a,b), (3.10), and replacing $\mathcal{V}(z)$ with the initial and final states, we obtain:

$$\left\{-iv\frac{\partial}{\partial z}+H_T(z)+V\right\}\left|\psi_\beta^{\pm}(z)\right\rangle = 0 \quad \Rightarrow \frac{\partial}{\partial z}\left|\psi_\alpha^{+}(z)\right\rangle = -\frac{i}{\mathrm{v}}\left(H_T+V\right)\left|\psi_\alpha^{+}(z)\right\rangle \tag{3.18a}$$

and

$$\left\{-iv\frac{\partial}{\partial z}+H_T(z)\right\}|\beta(z)\rangle=0\Rightarrow\frac{\partial}{\partial z}|\beta(z)\rangle=\frac{i}{\mathrm{v}}H_T|\beta(z)\rangle \tag{3.18b}$$

Thus, the transition amplitude takes the form:

$$\begin{aligned}a_{\beta\alpha}&=\delta_{\beta\alpha}-\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\beta(z)\left|H_T+V-H_T\right|\psi_\alpha^+(z)\right] && (3.19a)\\&=\delta_{\beta\alpha}-\frac{i}{\mathrm{V}}\int_{-\infty}^{+\infty}dz\left[\beta(z)|V|\psi_\alpha^+(z)\right] && (3.19b)\end{aligned}$$

From the Lippman-Schwinger equations (2.1a,b) and the expression (3.16) of the transition amplitude $a_{\beta\alpha}(\vec{\rho})$, this latter is written in other forms:

$$\begin{aligned}a_{\beta\alpha}(\vec{\rho})&=\delta_{\beta\alpha}-\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\beta(z)|V|\psi_\alpha^+(z)\right] && (3.20a)\\&=\delta_{\beta\alpha}-\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)|V|\alpha(z)\right] && (3.20b)\\&=\delta_{\beta\alpha}-\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)\left|V-VG_T^+V\right|\psi_\alpha^+(z)\right] && (3.20b)\end{aligned}$$

By replacing $|\alpha(z)\rangle$ in (3.20b) with the form given by the Lippman-Schwinger equation (3.8a), we obtain:

$$\begin{aligned}a_{\beta\alpha}(\vec{\rho})=&\delta_{\beta\alpha}-\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)|V|\psi_\alpha^+(z)\right]\\&+\frac{i}{\mathrm{v}}\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)|V|\int_{-\infty}^{+\infty}dz'G_T^+\left(z-z'\right)V\left(z'\right)\psi_\alpha^+\left(z'\right)\right]\end{aligned} \tag{3.21}$$

And subsequently, using the relations (3.20a,b) and (3.21), it follows in a completely analogous way to the establishment of the quantum variational form (2.8):

$$a_{\beta\alpha}(\vec{\rho})=\frac{\left(-\frac{i}{\mathrm{v}}\right)\int_{-\infty}^{+\infty}dz\left[\beta(z)|V|\psi_\alpha^+(z)\right]\left(-\frac{i}{\mathrm{v}}\right)\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)|V|\alpha(z)\right]}{\left(-\frac{i}{\mathrm{v}}\right)\int_{-\infty}^{+\infty}dz\left[\psi_\beta^-(z)\left|V\left\{\left|\,\psi_\alpha^+(z)\right]-\int_{-\infty}^{z}dz'G_T^+\left(z-z'\right)V\left(z'\right)\right|\psi_\alpha^+\left(z'\right)\right\rangle\right]\right\}} \tag{3.22}$$

Finally, if we adopt the notation (|) which indicates that the integration is performed over the electronic coordinates as well as the coordinate Z of $\vec{R}$, i.e., $(k|\Theta|k') = \int_{-\infty}^{+\infty} dz\,[k|\Theta|k']$ where Θ denotes an operator, and for cases where $\alpha \neq \beta$, the expressions (3.20a,-c) and (3.22) can be written in a condensed form:

$$a_{\beta\alpha}(\vec{\rho}) = -\frac{i}{\mathrm{v}}\left(\beta|V|\psi_\alpha^+\right) \tag{3.23a}$$

$$= -\frac{i}{\mathrm{v}}\left(\psi_\beta^-|V|\alpha\right) \tag{3.23b}$$

$$= -\frac{i}{\mathrm{v}}\left(\psi_\beta^-\left|V - VG_T^+V\right|\psi_\alpha^+\right) \tag{3.23c}$$

Now, from these three forms of $a_{\beta\alpha}(\vec{\rho})$ and in a completely analogous way to the establishment of the variational form (2.8) in the case of a direct collision (a single rearrangement channel), we obtain the variational transition amplitude in its so-called eikonal form of Schwinger's variational principle, namely:

$$a_{\beta\alpha}(\vec{\rho}) = \frac{\left(-\frac{i}{\mathrm{v}}\right)\left(\beta|V|\psi_\alpha^+\right)\left(-\frac{i}{\mathrm{v}}\right)\left(\psi_\beta^-|V|\alpha\right)}{\left(-\frac{i}{\mathrm{v}}\right)\left(\psi_\beta^-\left|V - VG_T^+V\right|\psi_\alpha^+\right)} \tag{3.24}$$

which is stationary for small arbitrary variations of the scattering states $|\psi_\alpha^+\rangle$ and $|\psi_\beta^-\rangle$ around their exact values. And since these scattering states are not known exactly, in a manner almost similar to the one previously established in Chapter 2, we arrive at an approximate form of the variational transition amplitude $\tilde{a}_{\beta\alpha}(\vec{\rho})$:

$$\tilde{a}_{\beta\alpha}(\vec{\rho}) = \left(-\frac{i}{\mathrm{v}}\right)\frac{\left(\beta|V|\tilde{\psi}_\alpha^+\right)\left(\tilde{\psi}_\beta^-|V|\alpha\right)}{\left(\tilde{\psi}_\beta^-\left|V - VG_T^+V\right|\tilde{\psi}_\alpha^+\right)} \tag{3.25}$$

During the expansion of the approximate scattering states $|\,\tilde{\psi}_\alpha^+\big)$ and $\left|\tilde{\psi}_\beta^-\right|$ on the truncated basis $\{i\rangle\}$ and $\{j\rangle\}$ respectively, the two basis sets are not necessarily identical, but they must have the same finite dimension N.

Then, by employing the stationarity condition, $\delta_{\tilde{a}_{\beta\alpha}}(\vec{\rho}) = 0$, we arrive at separating two finite series of linear equations for the expansion coefficients: one for $|\,\psi_\alpha^+)$ and the other for $\left|\psi_\beta^-\right|$. Solving these series of linear equations provides approximate solutions for $|\,\psi_\alpha^+)$ and $\left|\psi_\beta^-\right|$, denoted as $|\,\tilde{\psi}_\alpha^+\big)$ and $\big(\tilde{\psi}_\beta^-\,|$.

Finally, replacing the scattering states $|\,\psi_\alpha^+)$ and $\langle\psi_\beta^-|$ with their approximate expressions in equation (3.25) leads to the following more practical form of the transition amplitude:

$$\tilde{a}_{\beta\alpha}(\vec{\rho}) = \left(-\frac{i}{\mathrm{v}}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} (\beta|V|i) \left(D^{-1}\right)_{ij} (j|V|\alpha) \tag{3.26}$$

where $\left(D^{-1}\right)_{ij}$ is the (i,j) element of the matrix D^{-1}, the inverse of the matrix D defined by the element:

$$D_{ji} = \left(j\left|V - VG_T^{+}V\right|i\right) \tag{3.27}$$

Remark:

Note that all the target states have been taken into account in the representation of the Green's operator. We have also found a way to include all the states of the discrete spectrum and those of the continuum.

When developing the approximate scattering states $\left|\widetilde{\psi}_{\alpha}^{+}\right\rangle$ and $\left|\widetilde{\psi}_{\beta}^{-}\right|$, we have chosen a basis consisting only of the set of target states (discrete spectrum) and have ignored the inclusion of capture states on the projectile. This assumes that the effect of the coupling between capture and excitation, which exists in the energy domain of interest, must be weak for the variational principle to remain valid. This is true when the charge of the projectile is lower than that of the target nucleus.

To evaluate the variational transition amplitude, two types of matrix elements must be computed:

- Matrix elements of type $(j|V|i)$, called Born-I.
- Matrix elements of type $\left(j\left|VG_T^{+}V\right|i\right)$, called Born-II.

3.3 From the eikonal transition amplitude to the total excitation cross-section

In this section, we are going to determine the simplified forms of the transition amplitude and the total cross-section for the excitation of an atom by the impact of a proton or a bare ion, using the variational amplitude obtained within the impact parameter formalism.

3.3.1 Eikonal Transition Amplitude:

Indeed, the quantum transition amplitude corresponding to the process $\alpha \rightarrow \beta$ is given by:

$$T_{\beta\alpha} = \langle \beta | V \left| \psi_\alpha^+ \right\rangle \tag{3.28}$$

At first order in $\frac{1}{\mu}$, where μ represents the reduced mass of the colliding system, the scattering wave function is written as [46] [47]:

$$\psi_\alpha^+(\vec{R}, \vec{x}) \approx e^{i\vec{k}_\alpha \cdot \vec{R}} \psi_\alpha^{+E}(\vec{\rho}, \vec{z}, \vec{x}) \tag{3.29}$$

where ψ_α^{+E} is the eikonal wave function.
Consequently, we obtain the quantum transition amplitude in its eikonal form, namely:

$$T_{\beta\alpha} = \int d\vec{R} d\vec{x} e^{i\vec{q}\cdot\vec{R}} \phi_\beta^*(\vec{x}) V(\vec{R}, \vec{x}) \psi_\alpha^{+E}(\vec{\rho}, \vec{z}, \vec{x}) \tag{3.30}$$

where $\vec{q}$ represents the momentum transfer which can be expressed through its two components, longitudinal and transverse, with respect to the initial velocity $\overrightarrow{\mathrm{v}}$, namely:

$$\vec{q} = \vec{k}_\alpha - \vec{k}_\beta \tag{3.31a}$$

$$\vec{q} = q_v \cdot \vec{v} + \vec{\eta} \tag{3.31b}$$

and $\vec{\eta}$ is the transverse momentum transfer such that $\vec{\eta} \cdot \overrightarrow{\mathrm{v}} = 0$.

In the center of mass frame, the conservation of energy is written as:

$$\frac{k_\alpha^2}{2\mu} + \varepsilon_\alpha = \frac{k_\beta^2}{2\mu} + \varepsilon_\beta \tag{3.32}$$

ε_α and ε_β denote the energies of the initial and final bound states, respectively.
It can be shown that for values of $\mu \gg 1$, the longitudinal momentum transfer takes the following form:

$$q_{\mathrm{v}} = \frac{\varepsilon_\beta - \varepsilon_\alpha}{\mathrm{v}} + O\left(\frac{1}{\mu}\right) \tag{3.33}$$

And using the relation $\vec{R} = \vec{\rho} + \vec{z}$, we obtain:

$$\vec{q} \cdot \vec{R} \approx \frac{\varepsilon_\beta - \varepsilon_\alpha}{\mathrm{v}} \mathrm{z} + \vec{\eta} \cdot \vec{\rho} \tag{3.34}$$

Now, by substituting this approximate expression of $\vec{q} \cdot \vec{R}$ into the transition amplitude given by relation (3.30), we obtain the following form:

$$T_{\beta\alpha}(\vec{\eta}) = \int d^2\vec{\rho} e^{i \cdot \vec{\eta} \cdot \vec{\rho}} \left(\beta|V|\psi_\alpha^{+E}\right) \tag{3.35}$$

where the eigenvectors $|\alpha\rangle$ and $|\beta\rangle$ satisfy the expression:

$$\langle \vec{x}, z \mid k\rangle = e^{-i \frac{\varepsilon_k}{\mathrm{v}} z} \phi_k(\vec{x}) \tag{3.36}$$

with $(k = \alpha, \beta)$ and the notation $(\ |\ |\ )$ indicates that the integration is performed over the electronic coordinates and the z-component of $\vec{R}$.

Thanks to the notation: $(k|\Theta|k') = \int_{-\infty}^{+\infty} dz\, [k|\Theta|k']$ where Θ denotes an operator, and for cases where $\alpha \neq \beta$, the expression (2.20a) then becomes:

$$a_{\beta\alpha}(\vec{\rho}) = -\frac{i}{\mathrm{v}} \left(\beta|V|\psi_\alpha^{+}\right) \tag{3.37}$$

Using expression (3.21a) and form (3.36), the transition amplitude in the iconal approximation becomes [5]:

$$T_{\beta\alpha}(\vec{\eta}) = iv \int d^2\vec{\rho} e^{i\vec{\eta} \cdot \vec{\rho}} \rho^{2i \frac{Z_P(Z_T - 1)}{\mathrm{v}}} a_{\beta\alpha}(\vec{\rho}) \tag{3.38}$$

Note that in this last expression, the contribution of the inter-aggregate potential (3.6), which translates into a phase factor $\rho^{2i \frac{Z_P(Z_T - 1)}{\mathrm{v}}}$ depending on the impact parameter, has been reintroduced.

3.4 Iconal Cross Sections:

For an excitation process, the differential cross-section is given by the relation:

$$\frac{d\sigma_{\beta\alpha}}{d\Omega} = \frac{\mu^2}{4\pi^2} \frac{k_\alpha}{k_\beta} |T_{\beta\alpha}(\vec{\eta})|^2 \tag{3.39}$$

where Ω is the solid angle " $\sin(\theta) d\theta d\phi''$.

In the case where the incident energy is much greater than the energy difference $(\varepsilon_\alpha - \varepsilon_\beta)$ between the target states $|\alpha\rangle$ and $|\beta\rangle$, and in the case of a small longitudinal momentum transfer ($\frac{k_\alpha}{k_\beta} \approx 1$), the expression (3.39) for the differential cross-section becomes, based on relation (3.32):

$$\frac{d\sigma_{\beta\alpha}}{d\Omega} = \left| \frac{\mu T_{\beta\alpha}(\vec{\eta})}{2\pi} \right| \tag{3.40}$$

Consequently, the total effective cross-section will be:

$$\sigma_{\beta\alpha} = \int_0^{2\pi} d\phi_\beta \int_0^{\pi} \sin(\theta_\beta)\, d\theta_\beta \left| \frac{\mu T_{\beta\alpha}(\vec{\eta})}{2\pi} \right|^2 \tag{3.41}$$

By differentiating $\vec{q}^2$ calculated from expressions (3.31a,b) and based on a case of small momentum transfer $\frac{k_\alpha}{k_\beta} \approx 1$, we can write:

$$\eta d\eta \approx \mu^2 \mathrm{v}^2 \sin(\theta_\beta)\, d\theta_\beta \tag{3-42}$$

Taking into account that $\phi_\beta \equiv \phi_\eta$, the total cross-section is written as:

$$\sigma_{\beta\alpha} = \int_0^{2\pi} d\rho_\eta \int_0^{+\infty} d\eta\eta \left| \frac{T_{\beta\alpha}(\vec{\eta})}{2\pi \upsilon} \right|^2 \tag{3.43}$$

Now, by replacing $T_{\beta\alpha}(\vec{\eta})$ with its expression (3.38), and applying the two-dimensional Fourier transform, we obtain:

$$\sigma_{\beta\alpha} = \int d^2\rho \left| a_{\beta\alpha}(\vec{\rho}) \right|^2 \tag{3.45}$$

And since the system exhibits azimuthal symmetry, the total cross-section becomes:

$$\sigma_{\beta\alpha} = 2\pi \int_0^{+\infty} d\rho\rho \left| a_{\beta\alpha}(\vec{\rho}) \right|^2 \tag{3.45}$$

This expression determines the total effective cross-section for an excitation process. It remains valid as long as the impact parameter method is justified.

It was previously emphasized that the amplitude $a_{\beta\alpha}(\vec{\rho})$ is variational, and that an approximate form denoted $\tilde{a}_{\beta\alpha}(\vec{\rho})$ is completely determined by expression (3.26) when the approximate scattering states are developed in a vector subspace of dimension N

3.5 Remark:

Since it $\tilde{a}_{\beta\alpha}(\vec{\rho})$ does not require any integration over the impact parameter $\vec{\rho}$, we were able to overcome a major difficulty, namely the divergence that appears in the evaluation of matrix elements of the type $(i|V|j)$ and $\left(i\left|VG_T^{+}V\right|j\right)$ between certain degenerate hydrogenoid states during a quantum calculation when integrating over the impact parameter $\vec{\rho}$.

Chapter 4

Evaluation of Born-type matrix elements for transition amplitude.

In order to determine the variational transition amplitude $\tilde{a}_{\beta\alpha}(\vec{\rho})$, it is essential to evaluate two categories of matrix elements:

- matrix elements of the type $(i|V|j)$, known as Born-I.
- matrix elements of the type $\left(i\left|VG_T^+V\right|j\right)$, known as Born-II.

The vectors $|i\rangle$ and $|j\rangle$ are solutions of the Schrödinger equation with the target Hamiltonian $\mathrm{H_T}$.

It is useful to recall that the notation $(\|)$ indicates that the integration is carried out over the z-component of $\vec{R}$ as well as over the electronic coordinates $\vec{x}$ of the target.

4.1 Calculation of Born-I matrix elements:

At the beginning, it should be noted that in the model introduced previously in Chapter 3, the matrix elements of the type $(i|V|j)$, called Born-1, are expressed by:

$$(i|V|j) = \int_{-\infty}^{+\infty} dz\langle i|V|j\rangle \tag{4.1}$$

where the vectors $|i\rangle$ and $|j\rangle$ are given by equations (3.10a,b), or in a more general form:

$$\langle\vec{x}, z \mid k\rangle = e^{-i\frac{\varepsilon}{v}z}\phi_k(\vec{x}) \text{ with } (k = i, j) \tag{4.2}$$

which allows us to write that:

$$(i|V|j) = \int_{-\infty}^{+\infty} dz \int d\vec{x} e^{i\frac{\varepsilon_i}{\mathrm{V}}z}\phi_i^*(\vec{x})V(\vec{R},\vec{x})e^{-\frac{\varepsilon_j}{\mathrm{V}}z}\phi_j(\vec{x}) \tag{4.3}$$

If we write:

$$W_{ij}(\vec{\rho},z) = \int d\vec{x} \quad \phi_i^*(\vec{x})V(\vec{R},\vec{x})\phi_j(\vec{x}) \tag{4.4}$$

The elements of the Born-I type will be given by:

$$(i|V|j) = \int_{-\infty}^{+\infty} dz e^{\frac{i\varepsilon_i-\varepsilon_j}{\mathrm{V}}z}W_{ij}(\vec{\rho},z) \tag{4.5}$$

Where ε_i and ε_j respectively denote the energies associated with the electronic states $|\phi_i\rangle$ and $|\phi_j\rangle$. On the other hand, and in Appendix 2, it is shown that $W_{ij}(\vec{\rho},z)$ can be written as follows:

$$W_{ij}(\vec{\rho},z) = e^{i(m_j-m_i)\phi_R}W_{ij}(\rho,z) \tag{4.6}$$

m_i and m_j respectively represent the magnetic quantum numbers of the states $|\phi_i\rangle$ and $|\phi_j\rangle$, and ϕ_R is the azimuthal angle relative to the impact parameter $\vec{\rho}$.

In what follows, and in order to simplify the writing, the dependencies on $\vec{\rho}$ (in modulus and in angle) will be implicit.

Let us recall first the various symmetry properties of the elements W_{ij} , which will be very useful in the development of simplified forms of the matrix elements to be treated numerically, and which will reduce the computation time as well as the memory space for storing results.

$$W_{ij}(z) = W_{ij}^*(z) \tag{4.7a}$$

$$W_{ij}(z) = W_{ji}(z) \tag{4.7b}$$

$$W_{ij}(-z) = (-1)^{l_i+l_j+m_i-m_j}W_{ij}(z) \tag{4.7c}$$

$$W_{-i,-j}(z) = (-1)^{m_i-m_j}W_{ij}(z) \tag{4.7d}$$

In this last expression, the indices −i, −j respectively mean the simultaneous change of m_i and m_j to $-m_i$ and $-m_j$.

It is also important to note that the use of these symmetry properties makes it possible to reduce the number of matrix elements to be calculated numerically, and to restrict the integration interval over z from $]-\infty,+\infty[$ to values of z > 0 only.

If we write:

$$d_{ij} = \frac{\varepsilon_i - \varepsilon_j}{\mathrm{v}} \tag{4.8}$$

it follows that:

$$(i|V|j) = \left[\int_{-\infty}^{0} dz + \int_{0}^{+\infty} dz\right] e^{id_{ij}z} W_{ij}(z) \tag{4.9}$$

Let us define the function $G_{ij}(x, y)$ as follows:

$$G_{ij}(x,y) = \int_{x}^{y} dz e^{id_{ij}z} W_{ij}(z) \tag{4.10}$$

Referring to the symmetry properties of the elements $W_{ij}(z)$ (4.7a-d), we deduce the following properties for the function G_{ij}:

$$G_{ij}(-x,-y) = (-1)^{l_i+l_j+m_i-m_j} G^*_{ij}(x,y) \tag{4.11}$$

$$G_{ij}(x,y) = G^*_{ji}(x,y) \tag{4.12}$$

where G^*_{ij} is the conjugate function of G_{ij}.
Consequently, expression (4.9) becomes:

$$(i|V|j) = G_{ij}(0,+\infty) + (-1)^{l_i+l_j+m_i+m_j} G^*_{ij}(0,+\infty) \tag{4.13}$$

where the integration interval $]-\infty,+\infty[$ is reduced to an integration over the interval $[0,+\infty[$.

Since we can define a simpler asymptotic form of $W_{ij}(\rho, z)$, denoted $W^{as}_{ij}(\rho, z)$, for a given impact parameter ρ and sufficiently large values of z (with z being positive), the calculation of $G_{ij}(0,+\infty)$ is simplified. We divided the integration interval over z into two: an interval $[0, \widetilde{z}_{ij}]$ as small as possible where the integration over z is performed numerically, and another $[\tilde{z}_{ij},+\infty[$ in which the integration is done analytically.

For a given transition $j \to i$, we can define an asymptotic region by the value $\widetilde{z}_{ij} \geq 0$ such that:

$$W_{ij}(\rho, z) \approx W_{ij}^{as}(\rho, z) \quad \left(z \geq \tilde{z}_{ij} \text{ and } \tilde{z}_{ij} \geq \frac{3}{2}\rho\right) \tag{4.14}$$

and therefore we will have:

$$G_{ij}(0, +\infty) = G_{ij}\left(0, \tilde{z}_{ij}\right) + G_{ij}^{as}\left(0, \tilde{z}_{ij}\right) \tag{4.15}$$

where

$$G_{ij}\left(0, \tilde{z}_{ij}\right) = \int_{0}^{\tilde{z}_{ij}} dz e^{i d_{ij} z} W_{ij}(z) \tag{4.16}$$

and

$$G_{ij}^{as}\left(\tilde{z}_{ij}\right) = G_{ij}^{as}\left(\tilde{z}_{ij}, +\infty\right) = \int_{\tilde{z}_{ij}}^{+\infty} dz e^{i d_{ij} z} W_{ij}^{as}(z) \tag{4.17}$$

The function $G_{ij}\left(0, \tilde{z}_{ij}\right)$ is computed numerically, while the function $G_{ij}^{as}\left(\tilde{z}_{ij}\right)$ is calculated analytically .

4.2 Calculation of Born-II matrix elements:

The major difficulty of the Schwinger variational principle lies in the evaluation of second-order matrix elements denoted $\left(i\left|V G_{T}^{+} V\right| j\right)$ and called Born-II elements.

In order to properly describe the physical processes, we focused all our efforts on a suitable representation of G_{T}^{+}; a necessary condition for the accurate evaluation of the elements $\left(i\left|V G_{T}^{+} V\right| j\right)$.

The subspace of states generated by the bases $|i\rangle$ and $|j\rangle$ must be carefully chosen to properly describe the scattering states. On the other hand, a poor representation of the operator G_{T}^{+} leads to an error in the calculation of these elements which significantly alters the transition amplitude and consequently the physical predictions.

Aware of this problem, we focused on developing an approach capable of properly describing the different physical phenomena. However, we have invested all our efforts, both analytical and numerical, to achieve an adequate description of G_{T}^{+} and consequently a better evaluation of the Born-II matrix elements.

$$G_{T}^{+}\left(z, z'\right) = \left(-\frac{i}{\mathrm{v}}\right) \exp\left(-\frac{i}{\mathrm{v}} \int_{z'}^{z} H_{T}(u) du\right) \theta\left(z - z'\right) \tag{4.18}$$

where $\theta\left(z-z'\right)$ is the Heaviside function.

Now, by substituting the form (4.18) of the operator G_T^+ into the matrix element $\left(i\left|VG_T^+V\right|j\right)$ and introducing the closure relations respectively for the discrete and continuum spectra:

$$\sum_{\nu}|v\rangle\langle v|=1 \text{ and } \int dv|v\rangle\langle v|=1 \tag{4.19}$$

we can then write:

$$\left(i\left|VG_T^+V\right|j\right)=\left|\sum+\iint_v(i|V|v)\left(-\frac{i}{\mathrm{v}}\right)\theta\left(z-z'\right)(v|V|j)\right. \tag{4.20}$$

The symbol $\lfloor\sum+\rfloor$ means the summation over all discrete states as well as those of the continuum of the target [7,38]. Just like the vectors $|j\rangle$, the vectors $|\nu\rangle$ have the form:

$$\langle\vec{x},z\mid k\rangle=e^{-i\frac{\varepsilon_k}{\mathrm{v}}z}\phi_k(\vec{x})\quad(k=v,j) \tag{4.21}$$

By expanding expression (3.20), and using the property of the θ function:

$$\theta\left(z-z'\right)=\begin{cases}1 & z\geq z'\\ 0 & z<z'\end{cases} \tag{4.22}$$

we can express the term $\left(i\left|VG_T^+V\right|j\right)$ in two equivalent forms:

$$\left(i\left|VG_T^+V\right|j\right)=\left(-\frac{i}{\mathrm{v}}\right)\left[\sum+\int\right]\int_{-\infty}^{+\infty}dze^{id_{iv}z}W_{i\nu}(z)\int_{-\infty}^{z}dz'e^{id_{vj}z'}W_{\nu j}\left(z'\right) \tag{4.23}$$

or

$$\left(i\left|VG_T^+V\right|j\right)=\left(-\frac{i}{\mathrm{v}}\right)\left[\sum+\int\right]\int_{-\infty}^{+\infty}dz'e^{id_{ij}z}W_{vj}\left(z'\right)\int_{z'}^{+\infty}dze^{id_{iv}z'}W_{iv}(z) \tag{4.24}$$

From expression (4.14), and by defining the asymptotic regions by the values $\widetilde{z}_{iv}$ and $\widetilde{z}_{vj}$, two cases can be considered:

- $\tilde{z}_{iv}>\tilde{z}_{vj}$: it is easier to use relation (3.23) in the calculation of the matrix elements $\left(i\left|VG_T^+V\right|j\right)$. Indeed, the integration over z is analytical beyond $\widetilde{z}_{vj}$, so as soon as

$z > \widetilde{z}_{vj}$ the double integration reduces to a single integral.

- $\widetilde{z}_{iv} < \widetilde{z}_{vj}$: in this case, it is advantageous to use the form (4.24). It should be noted that the use of the symmetry relations of W_{ij} (4.7a-d) and those of the elements $\langle i|VG_T^+V|j\rangle$, allow us to return to form (4.23), and
subsequently to set up a unique numerical processing program in order to calculate the matrix elements.

By considering only the case $\widetilde{z}_{iv} > \widetilde{z}_{vj}$, we then have:

$$\left(i\left|VG_T^+V\right|j\right) = \left(-\frac{i}{\mathrm{v}}\right)\left[\sum + \int\right]_v H_{ij}^v \tag{4.25}$$

with:

$$H_{ij}^v = \int_{-\infty}^{+\infty} dz e^{i\frac{\varepsilon_i-\varepsilon_v}{v}z} W_{iv}(\rho,z) \int_{-\infty}^{z} dz' e^{i\frac{\varepsilon_v-\varepsilon_j}{v}z'} W_{vj}\left(\rho,z'\right) \tag{4.26a}$$

or in another form:

$$H_{ij}^v = \int_{-\infty}^{+\infty} dz' e^{i\frac{\varepsilon_v-\varepsilon_j}{v}z'} W_{vj}\left(\rho,z'\right) \int_{z'}^{+\infty} dz e^{i\frac{\varepsilon_i-\varepsilon_v}{v}z} W_{iv}(\rho,z) \tag{4.26b}$$

Now, using the symmetry properties W_{ij} as well as that of the function $\mathrm{G_{ij}}$ defined by expression (4.10), we can write:

$$\begin{aligned} H_{ij}^v(-\infty,+\infty) = G_{vj}^*(0,+\infty)\left\{(-1)^{l_v+l_j+m_v-m_j}G_{iv}(0,+\infty) + (-1)^{l_i+l_j+m_i-m_j}G_{iv}^*(0,+\infty)\right\} \\ +H_{ij}^v(0,+\infty) + (-1)^{l_i+l_j+m_i-m_j+1}H_{ij}^{v^*}(0,+\infty) \end{aligned} \tag{4.27}$$

where

$$H_{ij}^v(0,+\infty) = H_{ij}^v\left(0,\tilde{z}_{ij}\right) + H_{ij}^v\left(\tilde{z}_{vj},\tilde{z}_{iv}\right) + H_{ij}^v\left(\tilde{z}_{iv},+\infty\right) \tag{4.28}$$

and the function H_{ij}^ν is defined as:

$$H_{ij}^v(x,y) = \int_x^y dz \quad e^{id_{ij}z} W_{iv}(z) G_{vj}(0,z) \tag{4.29}$$

Consequently, the integrals of expression (4.27) will have the following three characteristics:

(1) $H_{ij}^\nu\left(0,\widetilde{z}_{vj}\right)$ is the result of a numerical double integration.

(2) $H_{ij}^{v}\left(\widetilde{z}_{vj},\widetilde{z}_{iv}\right)$ is the result of a numerical single integration.
(3) $H_{ij}^{\nu}\left(\tilde{z}_{i\nu},+\infty\right)$ reduces to an analytical expression called "$H_{ij}^{v^{as}}\left(\tilde{z}_{iv}\right)$ defined as follows":

$$H_{ij}^{v^{as}}\left(\tilde{z}_{iv}\right)=\int_{\tilde{z}_{iv}}^{+\infty}dze^{id_{iv}z}W_{iv}^{as}(z)G_{vj}^{as}(z) \tag{3.30}$$

where $G_{vj}^{as}(z)$ is given by expression (4.17).
It is important to note that for very large values of ν, the principal quantum number of the states$|\nu\rangle$, rounding errors lead to instability in computation. Thus, to
Taking into account all the states of the discrete spectrum, we have sought a development method $\frac{1}{v^3}$ like the one introduced by Bethe and Salpeter [6], which allows us to limit the numerical calculations to not-too-high ν states and guarantees the stability of the results for each pair of states $|i\rangle$ and$|j\rangle$.

Our work is not restricted to discrete states; we have extended it to continuum states. It was therefore necessary to precisely determine the region of the continuum located above the ionization threshold that effectively contributes. This consists in determining the energy ε_v called the cutoff energy, the energy after which the contribution of continuum states becomes totally negligible (see chapter 5).

According to R. Schakeshaft [58], B. Lasri 1998 [33], B. Lasri, M. Bouamoud, and R. Gayet [35], this contribution from the continuum is weak but not negligible.

Based on the behavior of the radial function R_{vl} for large values of $\boldsymbol{\nu}$ with fixed l and $\nu\gg 1$, we show that H_{ij}^{v} can be approximated by the following expression:

$$H_{ij}^{v}=\frac{1}{v^3}\,\mathrm{Exp}\left\{-\frac{l(l+1)(2l+1)}{6v^2}\right\}\left[A+\frac{B}{v^2}\right] \tag{3.31}$$

where A and B denote constants depending on $|i\rangle$ and $|j\rangle$.
For sufficiently large values of $\boldsymbol{v}$, the exponential term equals 1 in expression (3.31), and consequently the sum over $\boldsymbol{\nu}$ becomes:

$$\sum_{v=\vartheta_0}^{+\infty}H_{ij}^{v}=H_{ij}^{v_0}+A\sum_{k=1}^{+\infty}\frac{1}{\left(v_0+k\right)^3}+B\sum_{k=1}^{+\infty}\frac{1}{\left(v_0+k\right)^5} \tag{3.32}$$

where the constants A and B are determined in detail in appendix 1-2. v_0: denotes the value of $\boldsymbol{\nu}$ from which the elements H_{ij}^{v} follow the v^{-3} law of expression (4.30).

Referring to the Riemann zeta functions $\zeta(3)$ and $\zeta(5)$, the summations over k can be written:

$$\sum_{k=1}^{+\infty} \frac{1}{(v_0+k)^3} = \zeta(3) - \sum_{k=1}^{v_0} \frac{1}{k^3} \tag{3.33a}$$

$$\sum_{k=1}^{+\infty} \frac{1}{(v_0+k)^5} = \zeta(5) - \sum_{k=1}^{v_0} \frac{1}{k^5} \tag{3.33b}$$

Chapter 5

Excitation of the Hydrogen Atom by Proton Impact at Intermediate Energies

5.1 Introduction

The past few years have seen very vigorous developments in the study of single-electron collision processes in intermediate velocity ranges. The collisions of multi-charged ions with atoms are being studied in many disciplines like plasma physics, biophysics, and astrophysics. The work in nuclear and biological physics with highly charged ion beams from accelerators has turned out to be a novel fascinating area of the physics of atomic collisions. Such collisions are also frequent in astrophysical environments – for instance, the plasma screening effects on resonant Compton scattering of photons by hydrogenic ions in Lorentzian astrophysical plasmas. [39]

In the case of Helium-like and Hydrogen-like ions, total excitation cross sections have been observed to saturate at increments with the neutral atom's nuclear charge. This has been observed experimentally Wohrer et al 1986 [66], Xu et al 1988 [67], Tiwari et al 1998 [62]. Phenomenon of growth saturation was modeled theoretically by Brendlé and Gayet 1985 [10], Bouamoud 1988 [7], Bouamoud and Gayet 1989 [18], Lasri, Bouamoud, and Gayet 2004 [35].

Due to the relative simplicity of the excitation and charge transfer processes that allow the population of excited states of the hydrogen atom colliding with protons, the **P-H** system has often been used to test various models and approximations in atomic collision theory.

Hydrogen emissions (Hydrogen-line) play a very important role in astrophysical interpretation and analysis, particularly Balmer-α (Hα at 656 nm) and Balmer-β (Hβ at 486 nm), which serve as detectors of auroral protons. The Balmer-α emission from non-radiative collisions around supernovae is important to understand, since at these impact velocities and in most theoretical approaches, proton impact excitation to levels $n = 2$ and $n = 3$ dominates electronic excitation [29, 32, 49].

$$\text{Balmer-}\alpha \text{ emission:} \quad \mathrm{H}^*(n = 3) \rightarrow \mathrm{H}^*(n = 2) + h\nu$$

Recently, the collision process between the hydrogen atom and protons has been extensively studied experimentally over a wide range of collision energies (Donnelly et al. 1991 [14], Hughes et al. 1992 [23], Detleffsen et al. 1994 [13], Gilbody 1995 [21], Higgins et al. 1996 [22], Werner and Schatner 1996 [64]). Since then, numerous intensive theoretical studies employing various models (Slim 1993 [59], Ramillon and McCarroll 1993 [53], Ford et al. 1993 [15], Slim and Ermolaev 1994 [60], McLaughlin et al. 1995 [50], Kuang and Lin 1996 [31], Brendan McLaughlin et al. 1997 [49], F. Martin 1999 [45],lasri(1998) [33],Lasri et al(2004) [35]) have been carried out to better understand the processes of capture, excitation, and ionization.

In this section, we aim to study the excitation mechanism of the hydrogen atom by proton impact at energies ranging from 1 keV to 200 keV in the laboratory frame, in order to make a meaningful comparison between our theoretical results and the experimental results of Park et al [52]. and Barnett et al. [2], obtained using a technique known as the energy-loss spectrometry method. This is a spectroscopic method based on analyzing the energy lost by incident protons after collision. We also compare our results with other results obtained from different theoretical models, among which we mention those based on the close-coupling method, which continues to attract significant interest from researchers around the world to this day.

5.2 Close Coupling methods :

Close Coupling is an approach widely used in various fields of collision physics and recognized as one of the most reliable theoretical methods. It has been applied mainly in the low- and intermediate-energy range, where multiple scattering effects are so significant that perturbative approaches are no longer valid. For ion-atom collision, the total collision wavefunction is usually developed as a linear combination of adiabatic atomic orbitals **AO** or adiabatic molecular orbitals **(MO)** with some appropriate translation factors. A single-center expansion **(SCE)** is no longer satisfactory outside the high-energy range, where electron capture plays an important role.

The development **(AO)** based on the eigenfunctions of the target and the projectile is adequate in the energy region where the speed of the projectile is comparable to that of the bound electron. Thanks to the rapid advancement of computers, the number of states used in the development has been significantly increased. Currently, it is possible to directly calculate the total ionization cross sections through a large number of pseudo-continuum states on both the target and the projectile. 5tochima 1993, 1994 [4, 17].

The time-dependent wave function, in the **S**ingle-**C**enter **E**xpansion **(SCE)** and the **T**wo-**C**enter **E**xpansion (TCE), is developed respectively and in a standard manner as follows:

$$\psi_{SCE}(\vec{r},t) = \sum_{i=1}^{N_T} a_i(t)\psi_i^T(\vec{r}_T,t) \tag{4.1}$$

$$\psi_{TCE}(\vec{r},t) = \sum_{i=1}^{N_T} a_i(t)\psi_i^T(\vec{r}_T,t) + \sum_{i=N_T+1}^{N} a_i(t)\psi_i^P(\vec{r}_P,t) \tag{4.2}$$

where $\psi_i^T(\vec{r}T,t)$ and $\psi i^P(\vec{r}P,t)$ denote the atomic orbital of the target and the projectile, respectively, with appropriate electronic translation factors. $\vec{r_T}$, $\vec{r}_P$, and $\vec{r}$ denote the electronic coordinates with respect to the nucleus of the target, the projectile, and the origin of the coordinate system, respectively.

In 1978, Shakeshaft [58] introduced a new version using a two-center expansion (**T**wo-**C**entre **E**xpansion, TCE), employing 35 hydrogenic states with $l \leq 2$ on each center. This approach is known as TCES (Two-Centre Expansion with Sturmian functions).

Recently, Ford et al. (1993) [15] developed the (**SCE**) method by including states with angular momenta greater than **l=6**.

Although the cross sections resulting from both the SCE and TCE methods are generally above the experimental data, their behavior closely resembles the average trend of the experimental cross sections.

Later, in 1994, Slim and Ermolaev [60] presented an asymmetric two-center expansion **TCE** consisting of 50 states on the target and only a dominant 1s capture state on the projectile; this approach is referred to as **TCE**. They observed that the excitation cross sections for the **n=2** level of the hydrogen atom by proton impact become unstable in two-center close-coupling calculations and showed that the use of pseudo-continuum states on each of the two centers produces false oscillatory structures.

In 1997, Toshima [11] demonstrated that the false oscillatory structure is caused by strong coupling between the pseudo-continuum states (discretized continuum states) of the projectile and the bound states of the target.

5.3 The Variational Approach Used in This Work:

Our work focuses on deriving, using our theoretical frame work, new and more precise total cross sections for the direct excitation of hydrogen atom when a proton of moderate energy impacts it, while also drawing attention to the subtle profound discrepancy between numerous theoretical investigations and the experimental data concerning them .

In several theoretical approaches, and during the evaluation of the scattering amplitude, there are two main sources of errors. Either in the choice of the appropriate approximation method for the calculation or in the use of an imprecise input wave function to describe the target. Recently, the variational model based on the fractional form of Schwinger's Variational Principle has proven successful with a good estimation of total effective cross-sections for the excitation of the **n=2** and **n=3** levels of the hydrogen atom by proton impact at intermediate energies. Our theoretical predictions remain in very good agreement with other theoretical and experimental results.

This variational method, which offers an interesting approach for calculating effective cross-sections of proton scattering by atoms, is widely adopted at intermediate energies and could then be applied to low energies. Such a method has the major advantage of being independent of the normalization chosen for the wave functions, which are only required in the interaction region. Despite these favorable characteristics, the Schwinger method was usually applied only to elastic scattering but rarely to the calculation of effective cross-sections for atomic excitation by electron impact.

To start with, let us take into account that we already have developed a systematic method for studying the excitation of the hydrogen atom by proton impact at intermediate speeds, keeping in mind that this model can be extended to other studies, such as the excitation of hydrogenoid atoms by ion impact at intermediate speeds where $Z_T \gg Z_P$.

let's recall that the variational transition amplitude of Schwinger is stationary with respect to small variations of the scattering states $|\psi_\alpha^+\rangle$ and $\left\langle\psi_\beta^-\right|$ around their exact values. However, an inaccurate evaluation of the Green operator G_T^+ means a poor evaluation of the second-order matrix elements $\left(i\left|VG_T^+V\right|j\right)$. which directly leads to fatal errors in the transition amplitude.

In what follows, and as a first illustration, we are interested on the excitation of the hydrogen atom by proton impact ($Z_P = Z_T = 1$) at energies ranging from 1 keV to 200 keV in the laboratory frame, with the aim of carrying out a detailed comparison between our results and the experimental data. [52], [2].

In 1984, Brendlé [10] developed this variational approach for the excitation of ions and atoms by the impact of bare nuclei at intermediate speeds using a basis composed only of two vectors representing the only initial and final states, although the choice of this basis did not exactly satisfy the asymptotic conditions and proved to be insufficient.

Additionally, Bouamoud [7, 18] adopted this variational method and developed a new computational code in Fortran that calculates the total excitation cross sections using a basis consisting of five target states, including only the contribution of the discrete spectrum of this target in the representation of the Green's operator.

In 1998, B. Lasri [33]expanded the 2-state basis to a 5-state basis by including the entire discrete spectrum of the target as well as that of the continuum. However, the contribution of continuum states to the total excitation cross sections turns out to be small but not negligible. Thus, to study the excitation of the $\mathrm{n} = 2, \mathrm{n} = 3$ levels of the hydrogen atom by proton impact, the scattering wave functions $|\psi_\alpha^+\rangle$et $\left|\psi_\beta^-\right\rangle$ have been developed on a basis composed of 5 states $\left\{1\ \mathrm{s},\ \mathrm{ns}, \mathrm{np}_{\mathrm{o},} \mathrm{np}_{\mathrm{t}_1}, \mathrm{np}_{-1}\right\}$.

In the present work, during the course of our development, we did not limit ourselves to a basis of five states; instead, we expanded this basis first to 10 and then to 14 states, in order to describe the scattering wave function adequately and in a more comprehensive manner. Consequently, the basis used for the excitation of the $n = 2$ level of the hydrogen atom by proton impact is:

$$\{1s, 2s, 2p_0, 2p_1, 2p_{-1}, 3s, 3p_0, 3p_1, 3p_{-1}, 3d_0, 3d_1, 3d_{-1}, 3d_2, 3d_{-2}\}.$$

On the other hand, to study the excitation of the $n = 3$ level, we initially considered it sufficient to use a basis consisting of only 10 states:

$$\{1s, 3s, 3p_0, 3p_1, 3p_{-1}, 3d_0, 3d_1, 3d_{-1}, 3d_2, 3d_{-2}\}.$$

The results we present here concern the excitation of the hydrogen atom by proton impact for the levels $\mathbf{n} = \mathbf{2}$ and $\mathbf{n} = \mathbf{3}$. For this purpose, a computer program was developed to calculate the total excitation cross sections by integrating over the impact parameter ρ using Simpson's method for the variational transition amplitude $\tilde{a}_{\beta\alpha}(\vec{\rho})$.

To achieve this, the Fortran-based calculation program is divided into two main parts:

- The first part allows for the determination of the $(i|V|j)$ elements, referred to as Born-I type, as well as the second-order elements $\left(i\left|VG_T^+V\right|j\right)$, referred to as Born-II type, for various states (i,j). These elements will be used subsequently to determine the D_j elements of the matrix D to be inverted, which is defined as:

$$D_{ji}=\left(j\left|V-VG_T^+V\right|i\right)$$

- The second part determines the matrix D to be inverted and then obtains the values of the variational transition amplitude $\tilde{a}_{\beta\alpha}(\vec{\rho})$, as given by equation (3-27), and consequently the total excitation cross sections after integration over the impact parameter ρ.

In the first case, using a 5-state expansion denoted as Schw55, we consider B_1 and B_2 as two basis sets where the five basis states used for the excitation of level $\mathbf{n}=\mathbf{2}$ and $\mathbf{n}=\mathbf{3}$ are:

$$\{1s,2s,np_0,np_{+1},np_{-1}\}$$

Thus, the matrix D to be inverted can be defined as follows:

$$\begin{array}{c c}
 & \begin{array}{ccccc} 1s & 2s & 2p_0 & 2p_{-1} & 2p_1 \end{array} \\
\begin{array}{c} 1s \\ 2s \\ 2p_0 \\ 2p_{-1} \\ 2p_1 \end{array} &
\begin{bmatrix}
X & X & X & X & \xi \\
 & X & X & X & \xi \\
 & & X & X & \xi \\
 & & & X & X \\
 & & & & \xi
\end{bmatrix}
\end{array}$$

Similarly, in a second case, the fourteen basis states used in our development for studying the excitation of the $n=2$ levels are:

$$\{1s,2s,2p_0,2p_1,2p_{-1},3s,3p_0,3p_1,3p_{-1},3d_0,3d_1,3d_{-1},3d_2,3d_{-2}\}.$$

This development, according to our new 14-state Schwinger approach, will be referred to as **Schw1414** throughout the remainder of this work. Consequently, the matrix D to be inverted is given as follows:

$$
\begin{array}{cc}
 & \begin{array}{cccccccccccccc} 1s & 2s & 2p_0 & 2p_{-1} & 2p_1 & 3s & 3p_0 & 3p_{-1} & 3p_1 & 3d_0 & 3d_1 & 3d_{-1} & 3d_2 & 3d_{-2} \end{array} \\
\begin{array}{c} 1s \\ 2s \\ 2p_0 \\ 2p_{-1} \\ 2p_1 \\ 3s \\ 3p_0 \\ 3p_{-1} \\ 3p_1 \\ 3d_0 \\ 3d_1 \\ 3d_{-1} \\ 3d_2 \\ 3d_{-2} \end{array} &
\begin{bmatrix}
X & X & X & X & \xi & X & X & X & \xi & X & X & \xi & X & \xi \\
 & X & X & X & \xi & X & X & X & \xi & X & X & \xi & X & \xi \\
 & & X & X & \xi & X & X & X & \xi & X & X & \xi & X & \xi \\
 & & & X & X & X & X & X & X & X & X & X & X & X \\
 & & & & \xi & \xi & \xi & \xi & \xi & \xi & \xi & \xi & \xi & \xi \\
 & & & & & X & X & X & \xi & X & X & \xi & X & 0 \\
 & & & & & & X & X & \xi & X & X & \xi & X & \xi \\
 & & & & & & & X & X & X & X & X & X & X \\
 & & & & & & & & \xi & \xi & \xi & \xi & \xi & \xi \\
 & & & & & & & & & X & X & \xi & X & \xi \\
 & & & & & & & & & & X & X & X & X \\
 & & & & & & & & & & & \xi & \xi & \xi \\
 & & & & & & & & & & & & X & X \\
 & & & & & & & & & & & & & \xi
\end{bmatrix}
\end{array}
$$

X: denote the elements to be calculated.
ξ: denote the elements deduced by symmetry rules.
The elements below the diagonal are all directly derived from the upper elements.

The elements below the diagonal are all directly deduced from the upper elements.

Once the elements $D_{ji} = \left(j\left|V - VG_T^{+}V\right|i\right)$ of the matrix $\mathbf{D}$ to be inverted are calculated, we can determine the value of the variational transition amplitude $\tilde{a}_{\beta\alpha}(\vec{\rho})$ (Eq. 3.27) and consequently deduce the total excitation cross section by integrating over the impact parameter ρ.

It is worth recalling one of the most important consequences of the symmetry operations, which significantly reduced the computational time. Thus, a 14×14 matrix that would normally require the calculation of 196 elements only needs 65 elements. This resulted in a considerable gain in computation time.

5.4 Resultats and discussions:

5.4.1 Excitation of the Level $n = 2$:

In our case, five theoretical approaches that directly stem from our new procedure have been addressed:

1. First-order Born approximation, denoted Born-I,
2. Second-order Born approximation, denoted Born-II,
3. Schwinger-Born approximation (Schw-B) where $\mathbf{B}_1 = \{|\alpha\rangle\}$ and $\mathbf{B}_2 = \{|\beta\rangle\}$,
4. Schwinger approximation with 5 basis states, denoted Schw55, after including the contribution of the target's continuum states.
   (The notation Schw55D refers to our theoretical results without the inclusion of the contribution from the target's continuum states).
   The two basis sets are: $\mathbf{B}_1 = \mathbf{B}_2 = \{|\alpha\rangle_1, |\beta\rangle\}$ and three degenerate states with $\{|\beta\rangle\}$, more precisely, $\mathbf{B}_1 = \mathbf{B}_2 = \{1s, ns, np_0, np_{+1}, np_{-1}\}$ in the case of the transition $1s \to n = \mathbf{2}, \mathbf{3}$.
5. . Schwinger approximation with 14 basis states, denoted Schw1414, where $B_1 = B_2 = \{1s, 2s, 2p_0, 2p_1, 2p_{-1}, 3s, 3p_0, 3p_1, 3p_{-1}, 3d_0, 3d_1, 3d_{-1}, 3d_2, 3d_{-2}\}$.

Let us highlight that in all of our Schw55 and Schw1414 computations, we included both the discrete spectrum and the target continuum.

These theoretical results were compared to the experimental data of Park et al. (1976) [52] (Figure 4-3), which were normalized to the Born approximation at 200 keV by Bates [3] for the state n=2, which means a value of$\sigma = 6.63 \times 10^{-17}$ cm^2 , and then renormalized to our theoretical results at 200 keV, multiplied by a factor of 0.91.

We also compared our results with the experimental results of Morgan et al. (1973), Detlefsen et al. (1994) [23], Higgins et al. (1996) [22, 51] (Fig. 4-1, Fig. 4-2), and with those of Barnett [2] (Fig. 4-4) obtained using spectroscopic measurement techniques; as well as with other recent theoretical results, among which we mention the following: Shakeshaft

(1978) [58], which were obtained using a two-centre expansion approach known as TCES (Sturmian Two-Centre Expansion), involving 35 hydrogen-like pseudo-states of the Sturmian type on each centre.

Lüde et al. (1982) [43] presented results obtained from a numerical solution of the time-dependent wave function within the impact parameter formalism, using an expansion over a pseudo-basis set of the Hylleraas type. This procedure will hereafter be referred to as TDSE (Time-Dependent Schrödinger Equation).

In 1994, Slim and Ermolaev [44] developed a new approach based on an asymmetric two-centre expansion consisting of 50 states on the target and a single 1s capture state on the projectile. In what follows, this approach will be referred to as TCE51.

In Tables 4-1, 4-2, 4-3, and 4-4, as well as in Figures 4-1, 4-2, 4-3, and 4-4, our various theoretical results for the total excitation cross sections of the $2s$, $2p$, and $n = 2$ states of the hydrogen atom by proton impact are presented. These results were obtained using the different theoretical procedures mentioned previously: Born-I, Born-II, Schwinger-Born (Schw-B), Schwinger55D (Schw55D), Schwinger55 (Schw55), and Schwinger1414 (Schw1414). They are compared with the available experimental data and with other theoretical model results cited above.

Excitation of the (1s, 2s) state of the hydrogen atom:

Table 5.1: Cross sections from various models for the excitation of the hydrogen atom (1s, 2s) state. All values are scaled to 10^{-17}

E (keV)	Exp. Morgan et al	Err. Morgan	Exp. Higins et al.	Err. Higins	Shakeshaft (TCES)	Lüdde et al (TDSE)	Ford (SCE)	Slim (TCE51)	Martin (CC)	Schw 55D	Schw 55	Born I	Schw 1414
2	-	-	-	-	-	0.12	-	-	-	0.48334	0.4833	0.48334	0.36372
4	-	-	-	-	-	0.47	-	-	-	1.5966	1.5966	1.5966	1.1556
5	0.5890	0.1626	-	-	-	-	-	-	-	-	-	-	-
6	0.6003	0.1586	-	-	-	0.93	-	-	-	2.268	2.268	-	1.7025
7	0.5928	0.1465	-	-	-	-	-	-	-	-	-	-	-
8	0.5587	0.1598	-	-	-	0.19	-	-	-	-	-	-	2.0348
9	6.0014	0.16012	-	-	-	-	-	-	-	-	-	-	-
10	0.515	0.16001	0.61	0.1	-	-	-	-	-	-	-	-	-
12	0.587	0.14675	-	-	-	-	-	-	-	2.7372	2.7372	4.4127	-
15	0.862	0.2155	-	-	0.88	-	0.95	-	-	2.7035	2.7294	-	2.4696
16	-	-		-	-	0.9		-	-	-	-	-	-
20	1.04	0.26	1.05	0.09	-	-	-	-	-	2.539	2.5562	-	2.4669
25	1.06	0.65	-	-	1.56	-		-	-	-	-	2.8839	-
30	-	-	1.25	0.11	-	-	1.8	1.73	1.91	2.1311	2.136	2.5245	2.1902
40	-	-	1.39	0.08	2.1	-		2.01	-	1.7744	1.7724	2.0149	1.886
45	-	-	-	-	-	-	1.76	-	-	1.6248	1.6203	1.8288	-
50	-	-	1.32	0.07	1.79	-	-	1.98	1.62	1.4937	1.4886	1.6738	1.6346
60	-	-	1.22	0.08	1.32	-	1.52	1.82	-	1.2877	1.284	1.4306	1.4289

65	-	-	-	-	-	-	-	-	-	1.2062	1.2025	1.3335	-
70	-	-	1.12	0.07	-		-	-	-	1.1352	1.1317	1.2486	-
75	-	-	-	-	1.19	-	-	1.58	-	1.0736	1.0706	1.739	-
80	-	-	1.04	0.07	-	-	1.24	-	-	1.0183	1.0155	1.1076	1.1296
85	-	-	-	-	-	-	-	1.41	-	0.9689	-	-	-
90	-	-	0.94	0.05	-	-	-	-	1	-	-	-	-
100	-	-	0.87	0.07	-	-	1.02	1.2	-	-	-	-	9.2902
105	-	-	-	-	-	-	-	-	-	0.81389	0.8115	0.8635	-
125	-	-	-	-	-	-	0.829	-	-	0.70299	-	0.73376	-
145	-	-	-	-	0.8	-	-	0.82	-	0.61914	0.6179	0.63795	-
150	-	-	-	-	-	-	0.694	-	-	0.6012	0.6001	0.6177	-
160	-	-	-	-	-	-	-	-	-	-	-	-	0.60211
200	-	-	-	-	0.49	-	0.519	0.56	0.501	0.4661	0.465	0.46935	0.48707

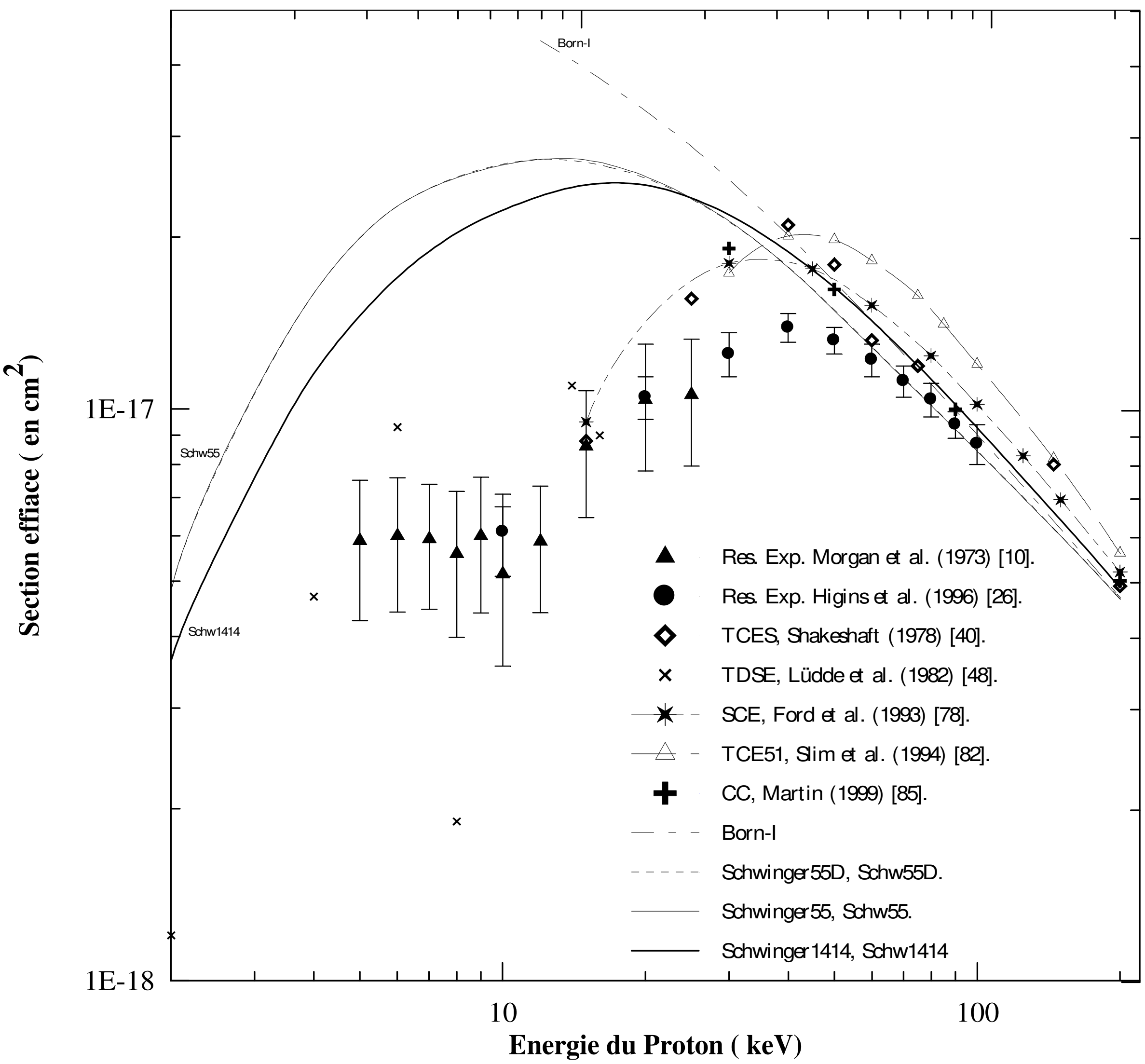

Figure 5.1: Total Excitation Cross Sections to the **2s** State of the Hydrogen Atom in 10^{-17} cm^2 by Proton Impact Compared with Various Theoretical and Experimental Results

Table 5.2: Total excitation cross sections to the 2p state of the hydrogen atom by proton impact (in cm^2). All values are scaled to 10^{-17}.

E (keV)	Exp. Morgan et al	Err. Morgan	Detlefsen et al.	Err. Detlefsen	Shakeshaft (TCES)	Lüdde et al (TDSE)	Ford et al (SCE)	Slim et al (TCE51)	Schw 55D	Schw 55	Born I	Schw 1414
10	-	-	-	-	-	-	-	-	-	-	-	1.7642
11	2.35	0.282	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	1.6124	1.6124	-	-
14	-	-	-	-	-	1.98	-	-	-	-	-	-
15	2.81	0.3372	-	-	2.46	-	2.58	-	1.8928	1.8808	-	2.4114
16	-	-	-	-	-	2.58	-	-	-	-	-	-
20	3.65	0.438	-	-	-	-	-	-	2.4694	2.4871	-	3.4292
25	-	-	-	-	4.85	6.58	-	-	-	-	-	-
30	5.5	0.66	-	-	-	-	5.78	6.82	4.1707	4.243	-	5.371
40	-	-	6.29	0.7548	6.89	-	-	8.04	5.9566	6.0525	-	6.7689
45	-	-		-	-	-	7.41	-	6.633	6.722	-	-
50	-	-	8.94	1.0728	6.88	-	-	8.39	7.101	7.1893	-	7.5804
60	-	-	9.25	1.11	7.29	-	7.92	8.42	7.6254	7.7055	-	7.9536
65	-	-	-	-	-	-	-	-	7.7346	7.8057	11.784	-
70	-	-	9.27	1.1124	-	-	-	-	7.7801	7.8437	11.371	-
75	-	-	-	-	7.97	-	-	8.22	7.7798	7.8365	10.986	-
80	-	-	8.66	1.0392	-	-	7.89	-	7.7463	7.7984	10.627	7.997
85	-	-	-	-	-	-	-	8.08	7.689	-	10.291	-

90	-	-	9.14	1.0968	-	-	-	-	-	-	-	-
100	-	-	8.21	0.9852	-	-	7.62	7.86	-	-	-	7.6528
105	-	-	-	-	-	-	-	-	-	7.3636	9.1415	-
120	-	-	8.12	97.44	-	-	-	-	-	-	-	-
125	-	-	7.17	86.04	-	-	7.13	-	6.9017	-	8.2274	-
140	-	-	7.26	-	-	-	-	-	-	-	-	6.7577
145	-	-	-	-	6.53	-	-	6.89	-	6.4971	-	-
150	-	-	7.2	86.4	-	-	6.64	-	6.3721	6.3928	7.3207	-
160	-	-	7.23	86.76	-	-	-	-	-	-	-	6.3197
175	-	-	6.74	80.88	-	-	-	-	-	-	-	-
180	-	-	6.83	81.96	-	-	-	-	-	-	-	-
200	-	-	6.36	76.32	5.55	-	5.79	5.91	5.4598	5.4688	6.0094	5.5997

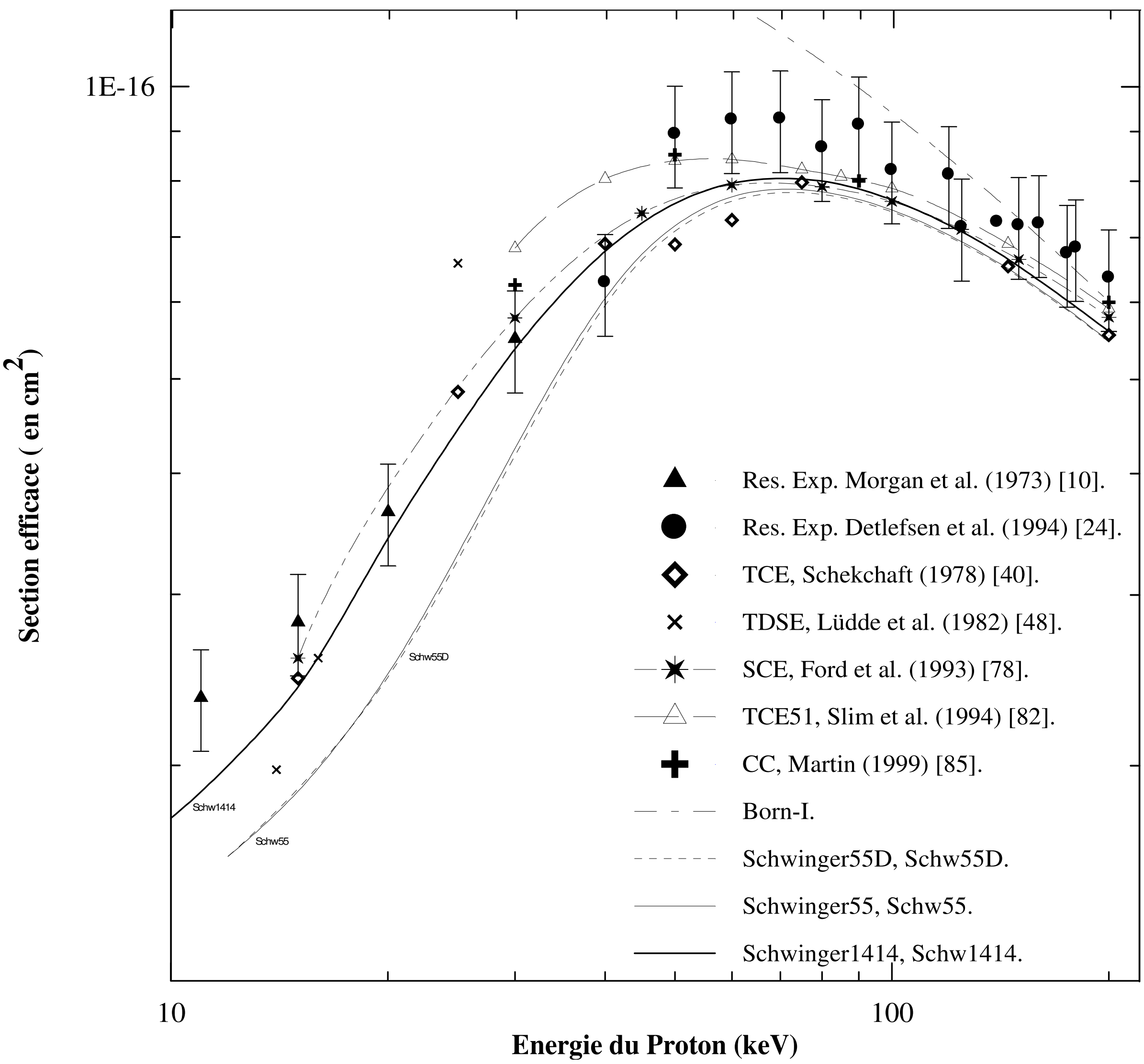

Figure 5.2: Total Excitation Cross Sections to the **2p** State of the Hydrogen Atom in 10^{-17} cm^2 by Proton Impact Compared with Various Theoretical and Experimental Results

Table 5.3: Total Excitation Cross Sections to the $n = 2$ Level of the Hydrogen Atom by Proton Impact (in 10^{-17} cm)

E (keV)	Exp. Park et al	Exp Barnett et al	Ford et al.	Lüdde et al (TDSE)	Born I	Born II	Schw-B	Schw55D	Schw55	Schw 1414
6	-	-	-	4.06	-	-	-	-	-	2.552734
8	-	-	-	2.67	-	-	-	-	-	3.247978
10	-	-	-	-	-	-	-	4.107596	4.1	3.790326
12	-	-	-	-	-	-	-	4.349572	4.349572	-
14	-	-	-	3.08	-	-	-	-	-	-
15	3.44±0.4	3.1213±0.4	3.53	-	-	-	-	4.596292	4.61019	4.880948
20	5.36±0.2	4.7502±0.4	-	-	-	-	-	5.00835	5.04321	5.8959
25	6.63±0.44	6.0424±0.4	-	-	-	-	-	5.585288	-	-
30	7.86±0.5	7.1799±0.4	7.58	-	-	-	-	6.30171	6.37903	7.56984
35	8.47±0.78	-	-	-	-	-	-	7.05283	-	-
40	9.64±0.83	8.7269±0.4		-	-	-	-	7.731	7.82491	8.65498
45	9.9±0.97	-	9.17	-	-	-	-	8.25778	8.34227	-
50	10.53±0.64	9.555±0.4	-	-	-	-	-	8.59475	8.67789	9.21497
55	10.59±0.25	9.737±0.4	-	-	-	-	-	8.80807	-	-
60	10.74±0.64	9.737±0.4	9.440001	-	-	-	-	8.91292	8.98945	9.38251
65	10.19±0.66	-	-	-	13.11764	-	-	8.94084	9.00817	-
70	10.26±0.84	9.373±0.4	-	-	12.62018	-	13.06544	8.91528	8.97543	-
75	10.26±0.27	-	-	-	12.16065	-	12.54475	8.85333	8.90713	-
80	9.75±0.38	8.8452±0.4	9.13	-	11.735	-	12.07277	8.7646	8.8197	9.12664

85	9.47±0.7	-	-	-	11.33971	-	11.64157	8.657946	-	-
95	9.32±0.55	-	-	-	10.62754	-	10.87887	8.412093	-	-
100	-	8.099±0.4	8.639999	-	-	-	-	-	-	8.582943
105	8.88±0.29	-	-	-	10.00498	11.67194	10.223	8.145659	8.175125	-
125	8.47±0.24	-	7.959	-	8.961185	10.21359	9.138772	7.604658	-	-
145	7.75±0.58	-	-	-	8.123102	9.10424	8.27584	7.094026	7.115095	7.420156
150	-	6.8068±0.4	7.334	-	7.93846	8.86623	8.086249	6.973273	6.992948	-
165	7.27±0.31	-	-	-	7.433435	8.226015	7.568416	6.6282	-	-
180	-	-	-	-	6.855059	7.510742	6.97635	6.210342	-	-

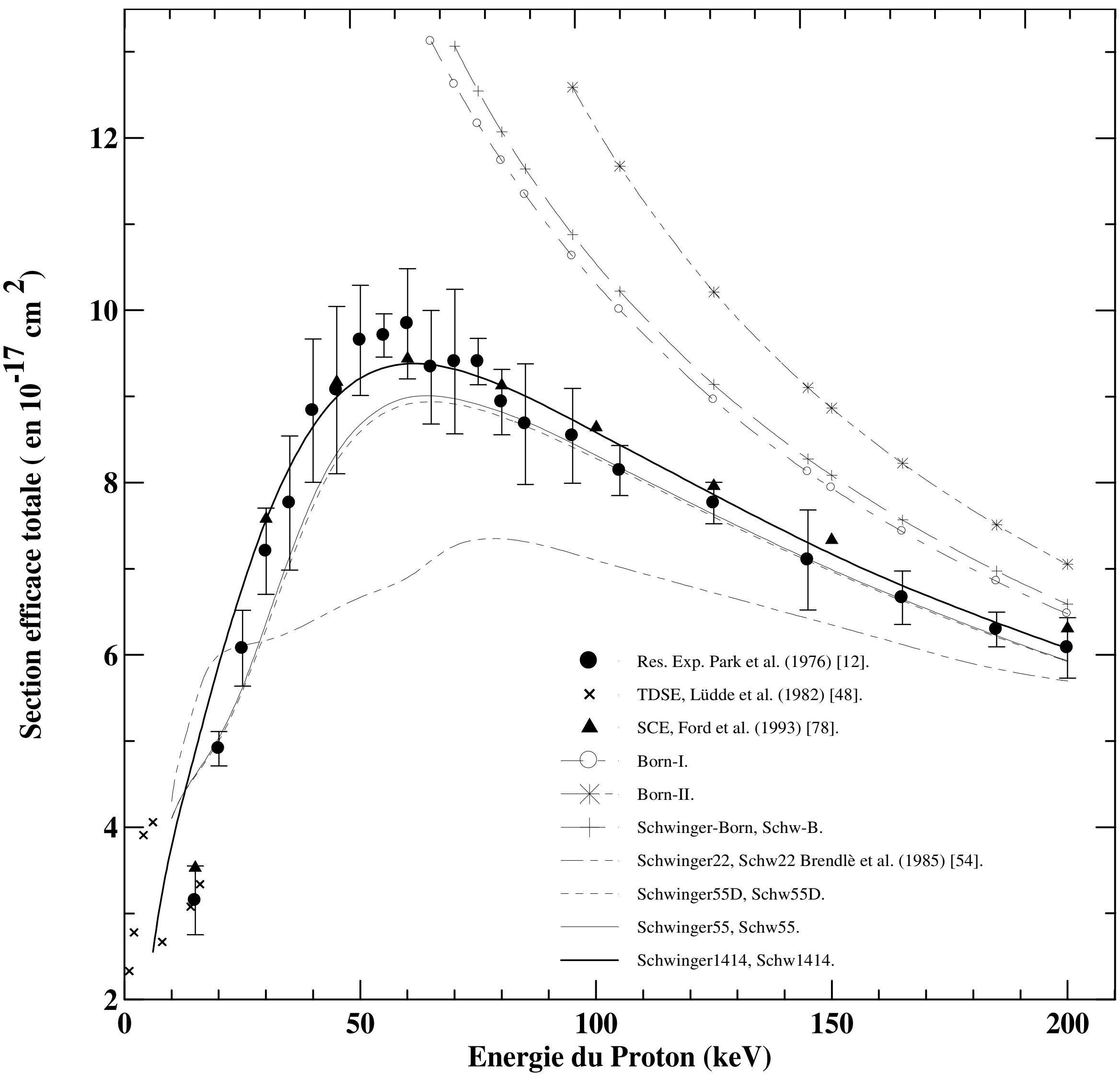

Figure 5.3: Total excitation cross sections of the hydrogen atom to the level n = 2 (in 10^{-17} cm^2), compared with the experimental results of Park et al.

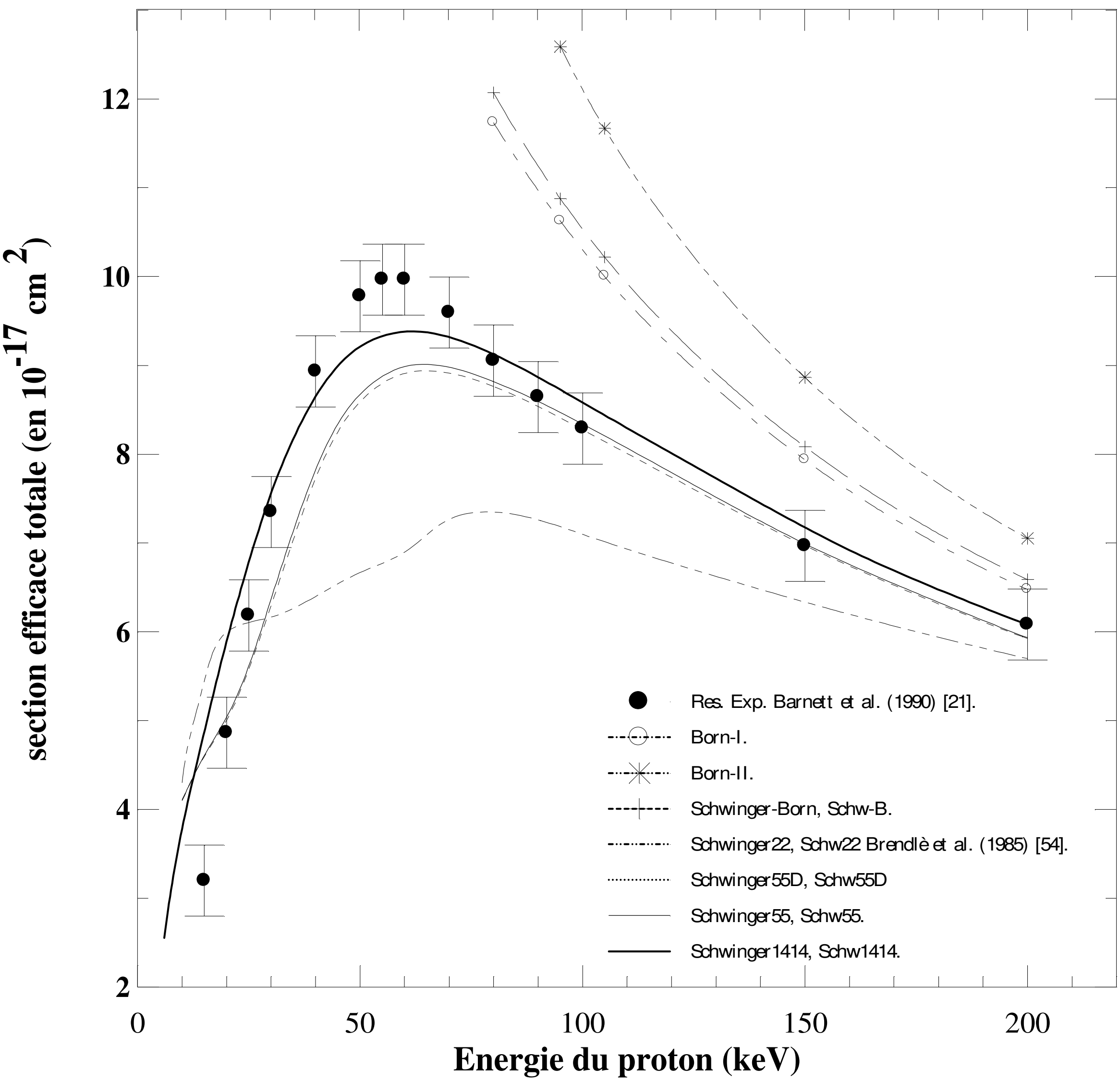

Figure 5.4: Total excitation cross sections of the hydrogen atom to the level n = 2 (in 10^{-17} cm^2), compared with the experimental results of Barnett et al.

5.4.1.1 Interpretation of the results

The total excitation cross sections of the $2s$, $2p$, and $n = 2$ states of the hydrogen atom by proton impact appear respectively in the previous tables ($4.1 \rightarrow 3$) as well as in the figures ($4.1 \rightarrow 3$), where they are compared with the available experimental data as well as with other results based on different theoretical procedures. Our present calculations are carried out with basis sets $\{|i\rangle\}$ and $\{|j\rangle\}$, initially composed of 5 basis states $\{1s, 2s, 2p_0, 2p_{+1}, 2p_{-1}\}$, then extended to 14 states $\{1s, 2s, 2p_0, 2p_{+1}, 2p_{-1}, 3s, 3p_0, 3p_{+1}, 3p_{-1}, 3d_0, 3d_{+1}, 3d_{-1}, 3d_{+2}, 3d_{-2}\}$. An automatic procedure was established to ensure greater accuracy.

In all the figures, our various results and theoretical predictions made with atomic-type basis sets are compared with several available experimental results such as those of Morgan et al. (1973) [51], Detlefsen et al. (1994) [13], and Higins et al. (1996) [22] for the $2s$ and $2p$ states, and those of Park et al. (1976) [52] and Barnett et al [25]. for $n = 2$ and $n = 3$. The comparison is mainly made around the maximum located near 40 keV, the range of intermediate energies where the coupling between excitation and capture channels occurs (Gayet, 1983) [17].

The present total excitation cross sections to the $2s$ state shown in $4 - 1$ and reproduced in the figure $4 - 1$ reveal that the Schw55 results, which refer to the 5-state Schwinger approach, show a peak around 12 keV, which significantly overestimates the total cross sections at low energy. However, expanding the basis from 5 to 14 states (Schw1414 results) introduced a slight shift of the peak to around 15 keV. But from 40 keV onward, both procedures converge almost similarly to the experimental data of Higgins et al [14]. as well as results obtained using various recent theoretical approaches: (TCES) Shakeshaft (1978) [58], (TDSE) Lüde et al. (1982) [43], (SCE) Ford et al. (1993) [15], (TCE51) Slim and Ermolaev (1994) [60], (CC) Martin (1999) [44].

The examination of Figure 4-2 and Table 4-2 related to the total excitation cross sections to the $2p$ state of the hydrogen atom by proton impact once again reveals that the effect of expanding the basis from 5 to 14 states is clearly visible. The results are comparable and sometimes significantly better than those given by various authors: Shakeshaft [58], Lüde et al. [43], Ford et al. (1993) [65], Slim and Ermolaev (1994) [60], and Martin (1999) [44].

Almost all theoretical predictions, except for the first Born approximation (Born-I), show reasonable agreement with the experiment for the excitation of the 2p state over a wide range of impact energies. Unlike the $2s$ excitation, the Schw55 cross sections for the $2p$ state are slightly smaller below 30 keV, while those of Schw1414 show very good agreement with the experiment. The TCE51 values remain consistently too large. This is mainly due to strong coupling between excitation and capture in the intermediate energy range. The first-order Born approximation (Born-I) agrees very well with experimental results beyond 80 keV, but is significantly higher at energies below 70 keV.

It is essential to note that the theoretical results provided by the first- and second-order Born approximations as well as the Schwinger-Born approximation greatly overestimate the total excitation cross sections of the $n = 2$ level in the low and intermediate energy ranges but show the same trend as experimental results at high energies. This indicates that excitation then becomes an independent channel and a direct process resulting from the interaction between the projectile and the active electron.

However, at energies below 40 keV, the multipole terms of the interaction contribute to the excitation of the 2p state, leading to contributions at smaller impact parameters. Consequently, the coupling influence between excitation and capture on the $2p$ excitation is no longer negligible. This influence could explain the underestimation of the total excitation cross sections of the 2p state given by Schw55 at energies below 40 keV.

During the development of the propagator in the matrix elements of Born-II, which appears in calculations based on the fractional form of the Schwinger variational principle where the basis was expanded from 5 states (Schw55) to 14 states (Schw1414), the results obtained by Schw1414 are significantly better than those by Schw55 and show very good agreement with almost all experimental results and with other results obtained from different theoretical models.

The contribution of the continuum near the ionization threshold to the total excitation cross sections is small. This allows us to conclude that the contribution of intermediate target states can be ignored, as was the case in previous applications (Brendlé et al. (1985) [10]; Bouamoud and Gayet (1989) [18]; Chabot et al. (1991) [11]). This conclusion gives more confidence in the results reported in these previous publications.

On the other hand, comparing experimental data with our cross sections for excitation of the $2s$ and $2p$ sublevels of hydrogen atoms by proton impact shows that the current fractional form application of the Schwinger principle must be limited to an impact energy range where the capture process is negligible. This is expected since the capture process is explicitly ignored in all Schwinger principle applications done so far. In the previous applications mentioned above, a neutral atom acted as the projectile. In that case, it is possible to use the present variational approach at intermediate impact velocities because electronic capture occurs, at minimum, as a two-step process (projectile ionization followed by electron transfer), whose probability is much smaller than that of one-step processes (Chabot et al. (1991) [11]).

For excitation of an H atom by a bare ion, the current variational approach can be improved by including at least one 1s capture state in the expansions of $|\psi_\alpha^+\rangle$ and $|\psi_\beta^-\rangle$.. Based on the TCE51 calculations by Slim and Ermolaev (1994) [59], a more significant improvement would come from accounting for the full continuum of intermediate states. However, due to scaling laws linked to the projectile's nuclear charge, our new theoretical approach remains a powerful tool to study excitation of Fe^{24+} and Kr^{34+} at 400 MeV and 34MeV/*nucleon* in collisions with various atoms. Therefore, the Born-I and Born-II matrix elements must be recalculated when the projectile's charge changes for a given target. Still, the variational principle should guarantee precise transition probabilities for all states included in the truncated basis on which $|\psi_\alpha^+\rangle$ and $|\psi_\beta^-\rangle$ are expanded.

5.4.2 Excitation of the level $n = 3$

It should be recalled that during a previous calculation (Lasri 1998) [33], which constituted the subject of a Magister thesis, and using a 5-state basis, we observed a shift toward lower energies, still following the same trend as the experimental results of Park et al. (1978) [52] and those of Barnett et al. (1990) [25].

This behavior can be explained by the fact that in the calculations of total excitation cross sections of the 3p state, the 5 basis states are $\{1S, 3S, 3\mathrm{p}_0, 3\mathrm{p}_{+1}, 3\mathrm{pp}_1\}$, but for the excitation of the 3d state, only the two-state variational approach was used, the initial and final states (Schw22). Thus, instead of inverting a matrix of order 5, we have a matrix of order 2.

Therefore, for the excitation to the 3 d_0 state, the basis will include $\{1S, 3\ \mathrm{d}_0\}$, and for the excitation to the 3 d_1, 3 d_{-1} , 3 d_2, and 3 d_{-2} states, the basis states are respectively $\{15, 3\ \mathrm{d}_1\}\, \{15, 3\ \mathrm{d}_{-1}\}\, \{1\ \mathrm{s}, 3\ \mathrm{d}_2\}\, \{1\ \mathrm{s}, 3\ \mathrm{d}_{-2}\}$.

What was concluded from this is that, in order to properly describe the excitation of the level $n = 3$, all intermediate states must be included; this led us to expand the basis to 10 states in order to obtain an adequate representation of the wave function. Thus, the basis will include: $\{1\ \mathrm{s}, 3\ \mathrm{s}_1 3\mathrm{p}_0, 3\mathrm{p}_1, 3\mathrm{p}_{-1}, 3\ \mathrm{d}_0, 3\ \mathrm{d}_1, 3\ \mathrm{d}_{-1}, 3\ \mathrm{d}_2, 3\ \mathrm{d}_{-2}\}$; and subsequently, the D matrix to be inverted can be written as follows:

$$\begin{array}{cc}
 & \begin{array}{cccccccccc} 1s & 3s & 3p_0 & 3p_1 & 3p_{-1} & 3d_0 & 3d_1 & 3d_{-1} & 3d_2 & 3d_{-2} \end{array} \\
\begin{array}{c} 1s \\ 3s \\ 3p_0 \\ 3p_1 \\ 3p_{-1} \\ 3d_0 \\ 3d_1 \\ 3d_{-1} \\ 3d_2 \\ 3d_{-2} \end{array} &
\left[\begin{array}{cccccccccc}
X & X & X & X & \xi & X & X & \xi & X & \xi \\
 & X & X & X & \xi & X & X & \xi & X & \xi \\
 & & X & X & \xi & X & X & \xi & X & \xi \\
 & & & X & X & X & X & X & X & X \\
 & & & & \xi & \xi & \xi & \xi & \xi & \xi \\
 & & & & & X & X & \xi & X & \xi \\
 & & & & & & X & X & X & X \\
 & & & & & & & \xi & \xi & \xi \\
 & & & & & & & & X & X \\
 & & & & & & & & & \xi
\end{array}\right]
\end{array}$$

The symmetry operations considerably reduced the computation time. Thus, for a 10×10 matrix, which would normally require the calculation of about a hundred elements, only 34 elements need to be computed, resulting in a significant saving in machine time.

The new results, referred to below as Schw1010, relate to our new variational procedure using a basis composed of 10 states for the excitation of the level $n = 3$ (1s $\to n = 3$). These results are presented in Table VI-4 and illustrated in Figures 4-5 and 4-6, where they are compared with the various available experimental results.

The experimental results of Park et al. (1978) [52] were renormalized using the same procedure described previously, by multiplying them by a factor of 0.925. The theoretical results obtained from various theoretical procedures cited so far include those of Shakeshaft (1978) [58], based on the TCE (Two-Centre Expansion) method using 35 hydrogen-like states with $l \leq 2$ on each center; those of Reading et al. (1981) [32], based on the SCE (Single-Centred Expansion) theoretical method in its various forms, OHCE (One and a Half Centred Expansion), namely the perturbative form POHC, or the unitary form UOHC.

We also compared our results with those provided by Lüde (1981) [43], using a semi-classical procedure called TDSE (Time Dependent Schrödinger Equation), and the recent results of Ermolaev et al. (1991) [15], TCAO (Two Center Atomic Orbital).

Table 5.4: Part 1 – Total Excitation Cross Sections to the $n = 3$ Level of the Hydrogen Atom by Proton Impact (in 10^{-17} cm^2)

E (keV)	Exp. Park et al	Exp Barnett et al	Park Norm	Shakeshaft (TCES)	Reading et al. (POHC)	Reading et al (UOHC)	Reading et al (SCE)
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-
15	1.1±0.5	1.09±0.4	1.00827	0.86	0.78	0.91	3.1
20	1.3±0.2	1.29±0.4	1.191592	-	-	-	-
25	1.55±0.2	1.53±0.4	1.420744	-	-	-	-
30	1.86±0.2	1.8±0.4	1.704893	1.8	1.8	1.6	2.7
35	2.11±0.3	-	1.934045	-	-	-	-
40	2.35±0.2	2.33±0.4	2.154031	-	-	-	-
45	2.52±0.2	-	2.309855	-	-	-	-
50	2.58±0.2	2.54±0.4	2.364851	-	-	-	-
55	2.59±0.2	-	2.374017	-	-	-	-
60	2.47±0.2	2.51±0.4	2.264024	2.1	2.1	2	2.2
70	2.59±0.2	2.42±0.4	-	-	-	-	-
75	2.31±0.2	-	2.117367	-	-	-	-
80	2.32±0.2	2.32±0.4	2.126533	-	-	-	-
85	2.47±0.4	-	2.264024	-	-	-	-
95	2.22±0.3	-	2.034872	-	-	-	-
100	-	-	-	1.5	1.7	1.7	1.7
105	2.13±0.3	-	1.952377	-	-	-	-
125	2.01±0.2	-	1.842384	-	-	-	-

145	1.72±0.3	-	1.576568	-	-	-	-
165	1.73±0.2	-	1.585734	-	-	-	-
185	1.38	-	1.26492	-	-	-	-
200	1.41	-	1.292419	-	-	-	-

Table 5.5: Part 2 – Total Excitation Cross Sections to the $n = 3$ Level of the Hydrogen Atom by Proton Impact (continued)

E (keV)	Ludde et al (TDSE)	Born-I	Born-II	S-B	Schw 55D	Schw 55	Schw 1010
1	0.04	-	-	-	-	-	-
2	0.03	-	-	-	-	-	-
4	0.15	-	-	-	-	-	0.589532
6	0.18	-	-	-	-	-	-
8	0.12	-	-	-	-	-	-
10	-	-	-	-	-	-	1.40447
14	0.49	-	-	-	-	-	-
15	-	-	-	1.423407	1.738419	1.862076	1.664672
20	-	-	-	1.984773	1.943322	2.068858	1.85552
25	-	-	-	2.411578	2.050087	2.175066	-
30	-	-	-	2.721797	2.098338	2.219837	2.045799
35	-	-	-	2.923836	2.109984	2.226436	-
40	-	3.153922	-	3.035077	2.098451	2.21	2.079762
45	-	2.997385	-	3.078195	2.072053	2.176702	-
50	-	2.854782	-	3.072709	2.036169	2.135075	2.053729
55	-	2.724985	-	3.035314	1.995012	2.088162	-
60	-	2.606696	-	2.976462	1.95042	2.037963	1.996003
70	-	2.399577	-	2.82463	1.857702	1.9.4953	1.924301
75	-	-	-	-	-	-	-

80	-	2.22451	-	2.657291	1.765705	1.83399	1.847372
85	-	-	-	-	-	-	-
95	-	2.007631	-	2.414259	1.63489	1.691028	-
100	-	-	-	-	-	-	1.69657
105	-	1.886481	3.105721	2.266423	1.554557	1.60378	-
125	-	1.68566	2.615784	2.009458	1.415709	1.45573	-
145	-	-	-	-	-	-	-
165	-	1.394767	1.990742	1.628507	1.197203	1.223062	-
185	-	1.285585	1.779237	1.486055	1.111372	1.132745	-
200	-	1.214787	1.648346	1.394621	1.054853	1.073547	1.159314

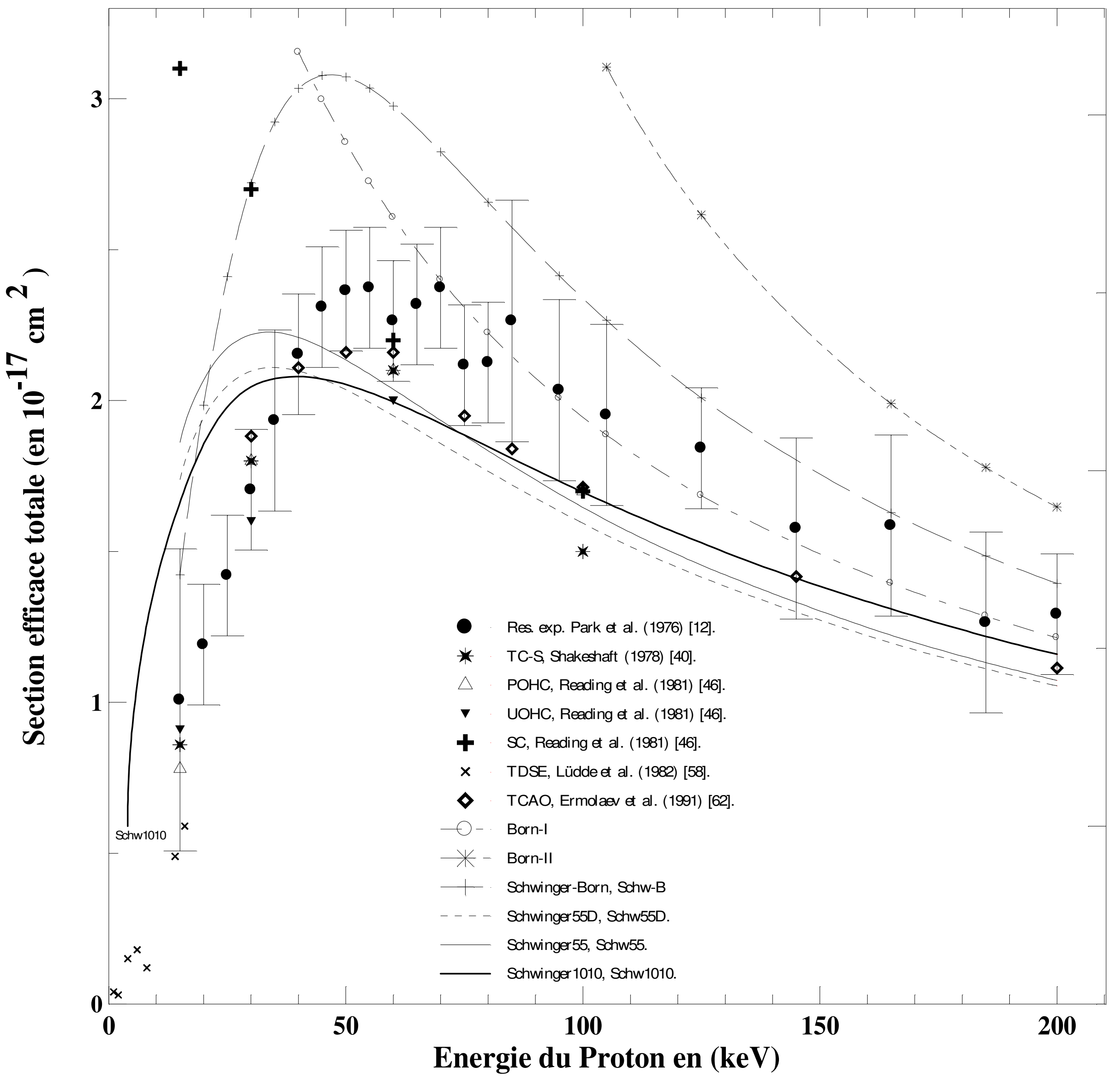

Figure 5.5: Total Excitation Cross Sections to the n=3 level of the Hydrogen Atom in 10^{-17}cm^2 by Proton Impact Compared with Various Theoretical and Experimental Results

The examination of the two preceding figures reveals a clear improvement compared to our previous calculations conducted in 1998 [33], with a slight shift toward lower energies while still following the same trend as the experimental results of Park et al. (1978) [52] and Barnett et al. (1990) [54]. Starting from 40 keV, a very good agreement is observed between the experimental data and the various theoretical predictions previously mentioned, based on different theoretical approaches (TC-S, POHC, UOHC, SCE, TDSE, TCAO). As for the results derived from Schw-B, they overestimate the experimental results despite having the same general trend with a peak around 50 keV, and the same applies to those of Born-I and Born-II, which also overestimate the various empirical results.

Regarding the various results obtained from different works carried out using various theoretical procedures, it can be said that the majority are in perfect agreement with the experimental results, except for those of SCE by Reading et al, which, below 50 keV, diverge by giving results significantly higher than the available experimental data.

In conclusion, it can be said that the decision to increase the basis on which the Green's propagator is expanded, from 5 states to 10 basis states, led to a better representation of the wave function and thus allowed us to obtain good results that remain in perfect agreement with the various available results, whether theoretical or experimental.

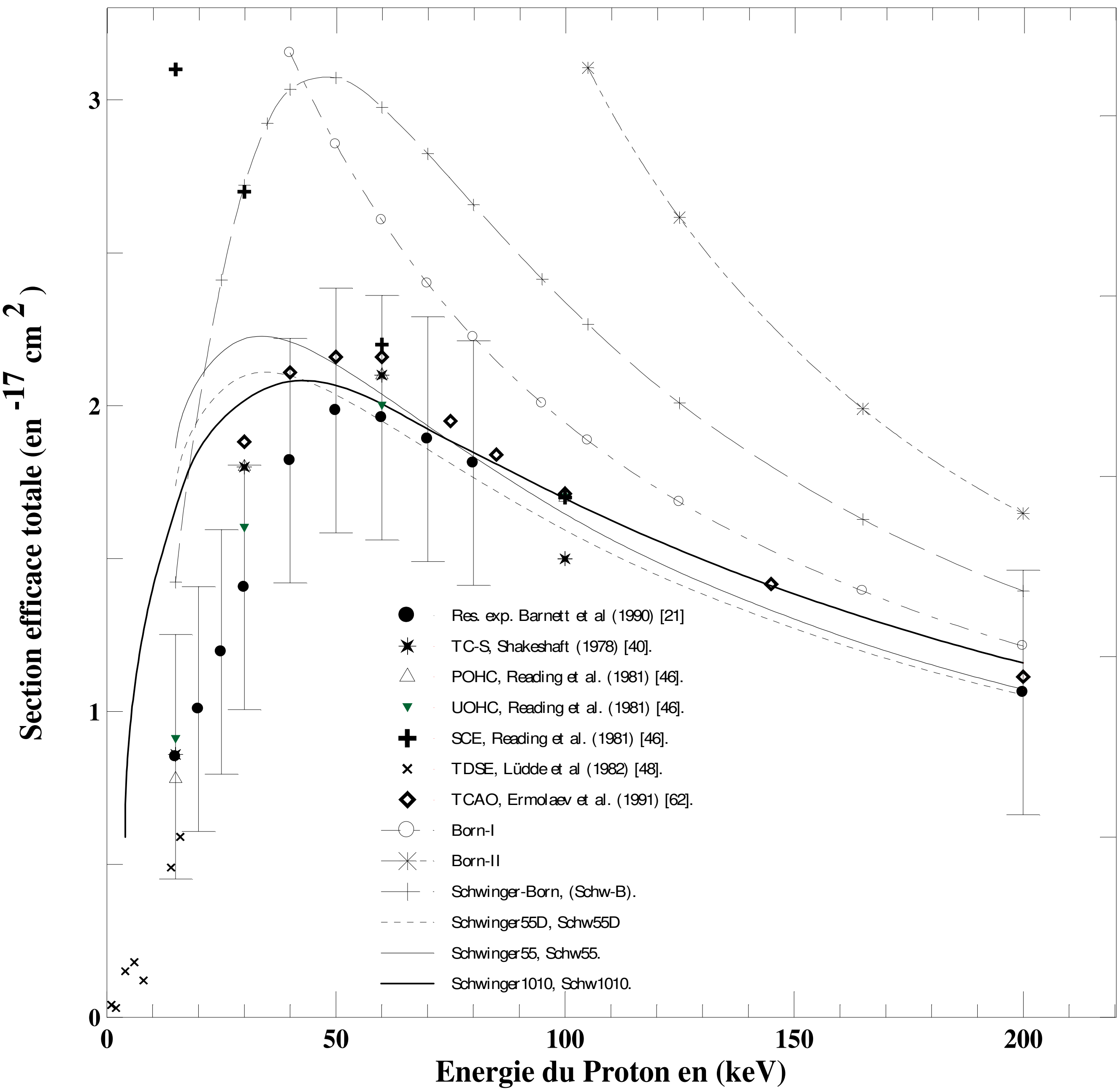

Figure 5.6: Total Excitation Cross Sections to the n=3 level of the Hydrogen Atom in $10^{-17}cm^2$ by Proton Impact Compared with Various Theoretical and Experimental Results.

General Conclusion

This thesis presented a variational approach based on the fractional form of the Schwinger variational principle to investigate the excitation of the hydrogen atom by proton impact in the intermediate energy range (1 keV to 200 keV). This system serves as a meaningful test case for the theoretical model, particularly in the regime where the coupling between excitation and capture channels is strong.

We have tried to improve the agreemcross-tween the excitation cross section data of the hydrogen atom by proton impact and our model using the variational impact parameter approach. Total excitation cross sections for transitions to the $n = 2$ and $n = 3$ states were computed and compared with available experimental data and theoretical models.

The results indicate that, in the energy range where the coupling is significant, projectile capture states can be effectively described by accurate continuum target states.

Finally, this variational approach will be able to become a powerful tool to investigate the excitation process in atomic collisions in the energy range from low to high energies. In particular, it remains a highly effective investigative tool for examining excitation processes in atomic collision studies within the intermediate impact velocity regime.

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Appendix A

Eikonal Approximation of the Target Green's Operator.

A.1 Eikonal form of Green's operator G_T^+

Analogous to the treatment of the Schrödinger equation for time-dependent collision theory [20][36], the following equation can be deduced in the eikonal approximation for the Green operator G_C^+ associated with the Hamiltonian H_C given by expression (II.1a). The eikonal operator verifies the equation:

$$\left[-i\,v\,\frac{\partial}{\partial z} \;+\; H_T(z)\right] G_T^+(z,\,z') \;=\; -\,\delta\big(z-z'\big) \tag{A.1}$$

wWhere$v$ is the impact velocity, and $H_T(z)$ is the target Hamiltonian, with the initial condition:

$$G_T^+(z,\,z') \;=\; 0 \quad \text{for} \quad z < z'\,. \tag{A.2}$$

Solving equation (A.1) without a second member gives

$$G_T^+(z,\,z') \;=\; \exp\!\Big\{-\,\tfrac{i}{v}\int_{z_0}^{z} H_T(u)\,du\Big\}\;G_T^+(z_0,\,z') \tag{A.3}$$

where z_0 is arbitrary subject to$z_0 > z'$.

Now, to solve the full equation (with the delta term), take

$$G_T^+(z,\, z') \;=\; \exp\Big\{ -\tfrac{i}{v} \int_{z_0}^{z} H_T(u)\, du \Big\}\; k(z_0,\, z')\,, \tag{A.4}$$

and vary the "constant" $k(z_0,\, z')$. By substituting (A.4) into (A.1), one finds

$$-\; i\, v\, \exp\Big\{ -\tfrac{i}{v} \int_{z_0}^{z} H_T(u)\, du \Big\}\; \frac{\partial}{\partial z}\, k(z_0,\, z') \;=\; -\,\delta\big(z - z'\big)\,, \tag{A.5}$$

which implies

$$k(z_0,\, z') \;=\; -\;\tfrac{i}{v}\;\exp\Big\{ \tfrac{i}{v} \int_{z_0}^{z'} H_T(u)\, du \Big\}\; \theta\big(z - z'\big)\,. \tag{A.6}$$

Hence, the eikonal approximation of the G_T^+ operator becomes:

$$G_T^+(z,\, z') \;=\; -\;\tfrac{i}{v}\;\exp\Big\{ -\tfrac{i}{v} \int_{z'}^{z} H_T(u)\, du \Big\}\; \theta\big(z - z'\big)\,, \tag{A.7}$$

where $\theta(z - z')$ is the Heaviside step function.

Appendix B

Analytical Evaluation of Coulomb Matrix Elements between Hydrogenic States.

B.1 Analytical Calculation of the Matrix Elements $W_{ij}(\vec{R})$

The elements $W_{ij}(\vec{R})$ are given by the following relationship:

$$W_{ij}(\vec{R}) = \int d\vec{x}\, \varphi_i^*(\vec{x}) V(\vec{R},\vec{x}) \varphi_j(\vec{x}) \tag{B.1}$$

where

$$V(\vec{R},\vec{x}) = Z_p \left[\frac{1}{R} - \frac{1}{|\vec{R}-\vec{x}|} \right] \tag{B.2}$$

and $\varphi_i(\vec{x})$ and $\varphi_j(\vec{x})$ denote hydrogenoid functions, generally given by:

$$\varphi_k(\vec{x}) \equiv \varphi_{n_k l_k m_k}(\vec{x}) = R_{n_k l_k}(x) Y_{l_k}^{m_k}(\hat{x}) \tag{B.3}$$

such that

$$R_{n_k l_k}(x) = e^{-\frac{Z_T x}{n_k}} \sum_{\mu=0}^{n_k - l_k - 1} B_{k\mu} x^{l_k+\mu} \tag{B.4}$$

where:

$$B_{k\mu} = \frac{1}{\sqrt{2}} \left[(n_k + l_k)!(n_k - l_k - 1)!\right]^{1/2} \frac{(2Z_T)^{(l_k+\mu+3)/2}}{n_k^{l_k+\mu+2}} \frac{(-1)^\mu}{(n_k - l_k - 1 - \mu)!(2l_k + 1 + \mu)!\mu!} \tag{B.5}$$

$Y_{l_k}^{m_k}(\hat{x})$ is a spherical harmonic:

$$Y_{l_k}^{m_k}(\hat{x}) = \left[\frac{2l_k + 1}{4\pi}\right]^{1/2} \left[\frac{(l_k - m_k)!}{(l_k + m_k)!}\right]^{1/2} (-1)^{m_k} P_{l_k}^{m_k}(\cos\theta_x) e^{i m_k \varphi_x} \tag{B.6}$$

with associated Legendre functions:

$$P_{l_k}^{m_k}(x) = (1 - x^2)^{m_k/2} \frac{d^{m_k}}{dx^{m_k}} P_{l_k}(x), \quad m_k \geq 0 \tag{B.7}$$

$$P_{l_k}^{-m_k}(x) = (-1)^{m_k} \frac{(l_k - m_k)!}{(l_k + m_k)!} P_{l_k}^{m_k}(x), \quad -m_k < 0 \tag{B.8}$$