Interferences in Electron Emission Spectra for H\textsuperscript{+} Impact on H\textsubscript{2}

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INTERFERENCES IN ELECTRON EMISSION SPECTRA
FOR H⁺ IMPACT ON H₂

by

Sabbir Hossain

A Dissertation
Submitted to the
Faculty of The Graduate College
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Sabbir Hossain
# TABLE OF CONTENTS

ACKNOWLEDGMENTS .................................................................................................. ii  
LIST OF TABLES ................................................................................................................ v  
LIST OF FIGURES ............................................................................................................... vi  
INTRODUCTION ................................................................................................................. 1  
THEORETICAL BACKGROUND .......................................................................................... 7  
  Ionization Mechanisms ................................................................................. 7  
The First Born Approximation ................................................................. 9  
Bethe Theory ................................................................................................. 11  
Electron Interference ................................................................................. 14  
First-order Interference ........................................................................... 15  
First-order Interference: Wave Optics Approach ................................... 20  
Second-order Interference ....................................................................... 21  
Second-order Interference: Wave Optics Approach ............................... 23  
EXPERIMENTAL PROCEDURE ................................................................................. 26  
  Ion Source and Accelerator ................................................................. 26  
  Scattering Chamber and Gas Target ................................................... 26  
  Data Acquisition and Spectrometer Control ....................................... 29  
  Angular Electron Spectrometer ............................................................. 31  
  Electron Detector .................................................................................... 35  
  Nozzle Position ............................................................................................ 36  
  Calibration of Voltage Divider ............................................................... 38  

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LIST OF TABLES

5.1 Values of the frequency parameter $c$ as a function of the electron emission angle $\theta$ for 1, 3, 5 MeV H$^+$ and 68 MeV/u Kr$^{33+}$ (Stolterfoht, 2003) projectiles impacting on H$_2$. The values of $\cos \theta$ are shown for comparison................................................................. 55

5.2 Values of the frequency parameter $c'$ and phase shift $\phi'$ as a function of the electron ejection angle $\theta$ for 1, 3, 5 MeV H$^+$ projectiles impacting on H$_2$ ........................................................................................................... 66
LIST OF FIGURES

2.1. Schematic for two- and three-body processes in ion-atom collisions............. 8

2.2 Triply-differential cross sections (TDCS) with respect to momentum
transfer $q$, energy $e$, and solid angle $\Omega$ of the ejected electron............... 13

2.3 Coordinates for a projectile $Z_\pi$ interacting with an electron on molecular
hydrogen (centers a and b).................................................................................. 16

2.4 Diagram of scattering kinematics.................................................................... 18

2.5 First-order interference deduced from wave optics..................................... 21

2.6 Schematic showing interference of the primary ejected electron wave of
amplitude $A_a$ from center $a$ with the secondary wave of amplitude $B_a$....... 24

3.1 Schematic drawing of the Western Michigan University tandem Van de
Graaff Accelerator and associated beam lines.................................................. 27

3.2 Schematic of scattering chamber (not to scale) and the collision region..... 28

3.3 Block diagram of the supporting electronics for spectrometer control
and data acquisition............................................................................................... 30

3.4 Schematic diagram of the parallel-plate angular electron spectrometer........ 32

3.5 Electron trajectory diagram for a parallel-plate spectrometer...................... 33

3.6 Parallel-plate electron spectrometer in low-resolution, high-energy
mode...................................................................................................................... 34

3.7 Typical channeltron electron detection efficiency as a function of
electron energy (eV) (Burle, Channeltron Handbook, 2002)......................... 36

3.8 Background electron counts as a function of nozzle position above the
beam axis (1 turn = 1.25 mm).............................................................................. 37

3.9 Electron emission from He showing a distinct Auger peak near 33 eV.... 38

4.1 Typical experimental data for 1 MeV $H^+$ on $H_2$ at 30° and 150°
observation angles............................................................................................... 40
List of Figures—continued

4.2 Target gas pressure dependence of the autoionization electron production for 3 MeV H⁺ on H₂................................................................. 41

4.3 Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 30°........... 45

4.4 Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 60°........... 46

4.5 Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 90°......... 47

4.6 Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 150°........... 48

4.7 Theoretical double differential cross sections (DDCS) for electron emission at 30°, 90°, and 150° angles in 3 MeV H⁺ on H₂ collisions .......... 49

5.1 Ratios of experimental and theoretical cross sections for electron emission by 1, 3, and 5 MeV H⁺ impact on H₂ for the electron observation angles indicated................................................................. 52

5.2 Experimental and theoretical values of the frequency parameter c ........... 56

5.3 Frequency parameter c extracted from the experimental fit values (see Table 5.1) displayed logarithmically as a function of collision velocity...... 57

5.4 Calculated double differential cross section (DDCS) ratios from Eq. 5.3 showing the expected interference structure resulting from the ionization of H₂ by 3 MeV H⁺ impact as a function of electron velocity..... 59

5.5 Calculated double differential cross section (DDCS) ratios from Eq. 5.3 for the ionization of H₂ by 1 and 5 MeV H⁺ impact as a function of electron velocity for angles 30°, 90° and 150°....................................................... 61

5.6 Ratios of the normalized differential cross section from Eq. 5.3 excluding the oscillatory term [1+sin(pd)/pd] (i.e., set to unity) evaluated with the effective charges $Z_e=1.19$ and $Z_t=1$ for molecular and atomic targets, respectively................................................................. 62

5.7 Relative contributions of dipole and binary transitions for the observation angles of 30°, 60°, 90° and 150°..................................................... 64

vii
List of Figures—continued

5.8 Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 30° ................................................................. 68

5.9 Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 60° ................................................................. 69

5.10 Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 90° ................................................................. 70

5.11 Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 150° ................................................................. 71

5.12 Cross section ratios of Fig. 5.8 divided by the corresponding fit curves, showing the existence of high-frequency oscillations ....................................................... 73

5.13 Cross section ratios of Fig. 5.9 divided by the corresponding fit curves, showing the existence of high-frequency oscillations ........................................ 74

5.14 Cross section ratios of Fig. 5.10 divided by the corresponding fit curves, showing the existence of high-frequency oscillations ........................................ 75

5.15 Cross section ratios of Fig. 5.11 divided by the corresponding fit curves, showing the existence of high-frequency oscillations ........................................ 76

5.16 Cross section ratios from Figs. 5.8, 5.9, 5.10, and 5.11 divided by the corresponding fits for 3 MeV H⁺ projectiles .......................................................... 77

A.1 Cross section ratios for 1 MeV H⁺ impact on H₂ at 30° electron observation angle compared with the fit (solid curve) obtained by the least square method ............................................................... 88

A.2 Cross section ratios compared with the fit (solid curve) obtained by the maximum likelihood method to obtain the frequency parameter c'. .......... 89
INTRODUCTION

In the collision of energetic ions with atoms or molecules, both elastic and inelastic processes can take place. Vast information is available on the energy and the angular distribution of the ejected electrons (Kuyatt et al., 1963, Stolterfoht et al., 1987, 1998, 1999). One of the basic inelastic processes, called direct ionization, involves the greatest exchange of energy and is also the most probable process for collision velocities exceeding the orbital velocity of the electron in the target (Rudd et al., 1992). The need to understand the ionization process is important in basic research in collision physics, radiation effects in biological and other materials, radiation detection devices, thermonuclear fusion, studies of surfaces and materials and also in the investigation of upper atmospheric phenomenon (Inokuti, 1971, Gealy et al., 1995).

Due to multielectronic effects and the multicenter character of molecular targets, ionization of such systems poses important difficulties in theoretical studies (Busnengo, 1998). However, H$_2$ is the simplest molecular target and for high impact collision energies, the vibrational and rotational motion of the molecule occurs on a much longer time-scale than the collision time, and, consequently the rotation and vibration of molecular nuclei during the collision can be ignored (Busnengo, 1998). Although the ionization of H$_2$ is a well understood process, phenomena associated with the indistinguishability of the atomic H centers remain a big challenge.

An interesting aspect of molecular ionization, not possible in atoms, is the possibility for interference effects when electrons are emitted coherently from identical atomic centers. This phenomenon is analogous to Young's two-slit
experiment (in the context of wave particle duality) with the slits replaced by the identical atomic centers of H$_2$. Hence, there is a simple interpretation in terms of wave optics. Young's two-slit experiment (Young, 1807), is often used as a prime example of quantum mechanics. As Feynman said, it "has in it the heart of quantum mechanics. In reality it contains the only mystery" (Feynman et al., 1965). While quantum mechanical interference is a consequence of the molecular structure, it can influence the dynamics of electrons that are ejected in collision events.

The overall ionization of H$_2$, mostly by fast charged particles (Kuyatt et al., 1963, Rudd et al., 1985, 1992, Lee et al., 1990), is well understood. However, interference effects have not been actively studied until the beginning of this decade. In the latter regard, the pioneering theoretical work of Cohen and Fano (Cohen and Fano, 1966) laid the foundation for ionization of the two-center molecular field by photons. Over last four decades, a large number of investigations of interference effects in H$_2$ for various collision systems (Tuan, 1960, Corchs, 1999, Walter, 1999) have advanced the understanding of Young type interference. The theoretical model developed by Briggs et al. (Briggs, 2001), analogous to that of Messiah (Messiah, 1970) and Moore (Moore, 1955) for coherent elastic scattering of electrons or x-rays by diatomic molecules, validated the evidence of oscillatory structure due to interference effects.

Recently, the first experimental evidence for interference effects has been found in the double differential ionization cross sections for electron emission from H$_2$ induced by 60 MeV/u Kr$^{34+}$ ($v_p \approx 50$ a.u.) ions (Stolterfoht et al., 2001). In this work, it was shown that the use of high velocity projectiles is important since it enhances interference effects. Data for 3 and 5 MeV H$^+$ ($v_p \approx 11$ a.u. and 14.2 a.u.,
respectively) impact show similar interference effects in electron emission from \( \text{H}_2 \) (Hossain et al., 2003).

Electron emission, depending on the projectile velocity, is found to be associated with particular ionization mechanisms. A simple two-body interaction occurs in a binary encounter collision involving a close interaction of a projectile and an electron, where the momentum transferred is large and the impact parameter is small. On the other hand, large impact parameter collisions with small momentum transfer at high projectile energies are three-body collisions (Stolterfoht et al., 1999). In this case, the interaction of fast ions with a target can be treated analogous to photoabsorption which is mediated by dipole transitions. Therefore, a fast projectile can be considered to act as a source of virtual photons. It has been shown that interference effects are due mainly to dipole transitions (Stolterfoht et al., 2001).

The experimental evidences concerning interference effects in electron emission from \( \text{H}_2 \) have spawned several theoretical investigations of this phenomenon (Nagy et al., 2002, Galassi et al., 2002, Sarkadi, 2003). In an extended model by Nagy (Nagy et al., 2002) using the straight-line version of the semi-classical approximation (SCA) for molecular targets the frequency of the oscillation is found to depend on the electron momentum component parallel to the beam direction. Galassi et al. (Galassi et al., 2002) developed a model, based on the continuum distorted wave-eikonal initial state (CDW-EIS) approximation, that also predicts a strong angular dependence (at forward and backward emission angles) of the interference effects.

Measurements for the collision system, 68 MeV/u \( \text{Kr}^{33+} \) ion on \( \text{H}_2 \) (Stolterfoht et al., 2003), exhibit a significant dependence of the interference structures on the electron emission angle, indicating a varying oscillation frequency. These results are
found to be consistent with the model of Nagy et al. and also with calculations based on the Born approximation (Crothers and McCann, 1983). Reasonable agreement has also been found between classical trajectory Monte Carlo (CTMC) results and this experimental data for krypton ion (Sarkadi, 2003).

Moreover, second-order interferences with higher frequency oscillations superimposed on the primary oscillatory structure have been observed (Stolterfoht et al., 2004). A theoretical formulation of these electron interferences based on wave optics suggests that the frequency doubling is a second-order effect in which the electron wave emitted at one center subsequently scatters at the other center and then interferes with the primary wave (Stolterfoht et al., 2004).

Interference effects in electron emission from H$_2$ have received wide attention in experimental studies by several investigators involving incident ions, electrons and photons. In the investigations of heavy molecules with synchrotron radiation, similar interference effects have been observed by photoionizing an inner shell of one atomic center followed by electron scattering at the other center (Mills et al., 1997, Heiser et al., 1997, Landers et al., 2001) and most recently in K-shell electron ejection from N$_2$ by incident photons (Rolles et al., 2003). In this latter work, the interference structure is attributed solely to second-order effects in which the ejected electron is scattered from the other center. Interference effects in electron emission from H$_2$ caused by C$_{6+}$ ions have been compared with the corresponding electron emission from atomic H targets for these same ions (Misra et al., 2004), and momentum-imaging techniques have been used to investigate both single- and double-ionization of H$_2$ by incident protons (Dimopoulou et al., 2003). Moreover, interferences have been observed in electron emission from D$_2$ (Frémont et al., 2003) and SF$_6$ (Mondal and Shanker, 2004) induced by incident electrons. Furthermore, interferences in the ionization of
one-electron $\text{H}_2^+$ is being studied in collisions of this ion with atomic He and Ar (Sulik et al., 2003).

In this present work, interference structures associated with coherent electron emission from $\text{H}_2$ are investigated for 1, 3, and 5 MeV $\text{H}^+$ impact. The measurements were performed at Western Michigan University using the tandem Van de Graaff accelerator. Cross sections for the ejection of electrons with energies of 3 - 300 eV were measured for observation angles ranging from 30° to 150° with respect to the incident proton direction. Normalization of the measured molecular cross sections to calculated atomic cross sections exhibits sinusoidal-like oscillations in the resulting ratios for electron energies less than ~ 250 eV. The observed interference phenomena reveal the existence of new, and, in the same cases, as yet unexplained features associated with the interference. While the present results exhibit the strong angular dependence of the interference features observed by Stolterfoht et al. (2003), they also display a previously unexplored dependence of the interference structures on the collision velocity. These results are used to parameterize the changing frequency of the oscillatory structure as a function of the collision velocity.

As in Stolterfoht et al. (2004), there are higher-frequency oscillations superimposed on the main structure attributed to interference of the primary wave with the secondary wave produced following scattering at the other atomic center. These second-order oscillations are found to exhibit only a small dependence on the electron observation angle and essentially no dependence on the collision velocity. Perhaps most interesting, however, is the evidence for still higher frequency oscillations (a factor of ~ 20) superimposed on second-order oscillations. Although the origin of these high-frequency oscillations is uncertain, a tentative explanation for
the high-frequency oscillations is given in terms of transient molecular formation with the incoming $\text{H}^+$ ion.
THEORETICAL BACKGROUND

Ionization Mechanisms

While the atomic ionization process is strictly a three-body problem, in ion-atom collision interactions ionization can be considered as a two-body problem, or a chain of two-body interactions, when the ion transfers significant momentum to an atomic electron with a negligible role played by the target nucleus (M. Gryznski, 1965). A simple two-body process occurs in a binary collision, i.e., the “close” interaction of a projectile and an electron, where the interaction of the ejected electron with the target nucleus is neglected. In this case, the momentum transferred from the projectile is given directly to the ejected electron. This basic idea was described analytically by Rutherford (1911), assuming that the target electron was initially at rest. The momentum transferred is large in binary collisions with relatively small impact parameters. This two-body binary process is analogous to the Compton scattering of photons and was recognized by Bethe (H.A. Bethe, 1930, 1997). This concept is schematically displayed in Fig. 2.1.

On the other hand, ionization in a three-body process involves a binary encounter followed by scattering of the outgoing electron in the Coulomb field of the target nucleus to balance the missing momentum. Thus, only small momentum is transferred from the projectile. In a three-body process low energy ejected electrons are affected most strongly by the target nucleus and this effect decreases with increasing electron energy. Soft collisions, a process attributed to three-body collisions involving the projectile, the active electron, and the residual target ion, occur with highest probability for high projectile energies with large impact
parameters and small momentum transfer (T.F.M. Bonsen, 1970, Y. K. Kim, 1972). For three-body processes the interaction of fast ions with a target can be treated analogous to photoabsorption which is mediated by dipole transitions, where the incident photon is annihilated. Therefore, a fast projectile can be considered to act as a source of virtual photons which gives rise to dipole transitions involving the transfer of a single unit of angular momentum, $\Delta l = 1$ (E. J. Williams, 1934). This three-body collision mechanism is also shown in Fig. 2.1 (Stolterfoht, 1999).

Figure 2.1: Schematic for two- and three-body processes in ion-atom collisions. Two-body processes are binary collisions analogous to Compton scattering where the target nucleus plays a negligible role. In three-body collisions, the active electron interacts with the target nucleus resulting in dipole transitions analogous to photon impact and annihilation.
It was shown in the pioneering work of Bethe (H.A. Bethe, 1930) and later derived by Fano (U. Fano, 1954), Miller and Platzman (Miller and Platzman, 1957) and Inokuti (M. Inokuti, 1971) that the Born approximation cross section for low energy electrons can be described by dipole-like transitions. Furthermore, the soft collision process contributes roughly half of the ejected electron intensity in the low-energy region ranging from zero energy to a value equal to the corresponding binding energy (Rudd et al., 1992). This, low-energy electron production involves a logarithmic projectile energy dependence ($\ln T/T$) resulting from the integration over the momentum transfer (Bethe, 1930, Fano, 1954, Inokuti 1971, Kim, 1972), where $T = E_p/M_p$ is the projectile energy reduced by the projectile mass $M_p$. Therefore, the double differential cross section (DDCS) for ejection of low-energy electrons can be expressed as:

$$\frac{d^2\sigma(\varepsilon \rightarrow 0)}{d\varepsilon d\Omega} = \text{const} \times \left(\frac{\ln T}{T}\right).$$

Hence, the Born approximation provides an adequate basis for the evaluation of differential cross sections for low-energy electrons by high energy projectiles.

The First Born Approximation

Within the framework of the Born approximation the ionization of a hydrogen-like 1s electron has been evaluated by several authors (Massey and Mohr 1933, Landau and Lifschitz 1958, Belkic’ 1978, Crothers and McCann 1983), with the double differential cross section written as

$$\frac{d^2\sigma}{d\varepsilon d\Omega} = (2\pi)^4 \frac{k}{v_p^2} \int d^2 \tilde{q}_\perp |T_{\varepsilon} (\tilde{q})|^2.$$  2.1

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where $e$ is the outgoing electron energy, the solid angle $\Omega$ refers to the direction of the ejected electron of momentum $\tilde{k}$ with $k = \sqrt{2e}$, $v_p$ is the velocity of the projectile and $\vec{q}_\perp$ is the transverse component of the momentum transfer, $\vec{q}$. The scattering matrix element $T_\theta$ in the Born approximation is

$$T_\theta(\vec{q}) = \langle \Phi_f^{PW} | V_p | \Phi_i^\beta \rangle$$ \hspace{1cm} (2.2)

where $V_p$ is the perturbing potential. To obtain the first-order Born approximation (the PWBA), the initial wave function $\Phi_i^\beta$ describes the electron bound to the target nucleus and $\Phi_f^{PW}$ is the final wave function described by a plane wave.

Since the majority of electrons ejected in soft collisions carry a relatively small momentum $k$ and consequently experience significantly the potential of the target nucleus, the final plane wave function needs to be modified to account for this attraction. The modified final wave function $\Phi_f^\beta$ is given by a Coulomb distorted plane wave (Salin, 1969) which can be expressed as

$$\varphi_f = \frac{e^{ik\cdot\vec{x}}}{(2\pi)^{3/2}} N\left(\frac{Z_T}{k}\right)F_1[-iZ_T/k;1;ikx-i\vec{k}\cdot\vec{x}],$$

where $\vec{x}$ is the electron-target nucleus position vector, $Z_T$ is the target nuclear charge, $N(\frac{Z_T}{k})$ is the normalization factor of the continuum wave function, and $F_1$ is the confluent hypergeometric function. Thus, the modified scattering matrix element can be written as

$$T_\theta(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \widetilde{V}_p(\vec{q})F(-\vec{q})$$ \hspace{1cm} (2.3)

where, $\widetilde{V}_p(q)$ is the Fourier transform of the perturbing potential $V_p(\vec{r}) = -Z_p/r$ ($Z_p$ is the projectile nuclear charge and $\vec{r}$ is the electron-projectile position vector) and $F(-\vec{q})$ is a form factor that depends on the momentum transfer $\vec{q}$. The transition amplitude $R_\theta$ as a function of $\vec{q}_\perp$ is given by
Then, combining Eqs. (2.1) and (2.4) the double differential cross section is obtained as

\[ \frac{d^2 \sigma}{d\omega d\Omega} = k \left| \frac{d^2 \omega}{dq^2} \right| R_{\gamma} (\vec{q}) \]

where the transition amplitude is \( R_{\gamma} (\vec{q}) \). Now, considering ionization from a 1s ground state, we obtain

\[ |R_{\gamma}|^2 = 4 |N(Z_{\gamma} / k)|^2 \exp \left[ -2(Z_{\gamma} / k) \tan \left( \frac{2Z_{\gamma} k}{Z_{\gamma}^2 + q^2 + k^2} \right) \right] \times \left[ \frac{Z_{\gamma}^2 + (q + k)^2}{Z_{\gamma}^2 + (q - k)^2} \right] R_{\gamma}^{PWBA} (\vec{q})^2, \]  

and the corresponding transition amplitude to the PWBA is given by

\[ R_{\gamma}^{PWBA} (\vec{q}) = i \frac{2^{5/2}}{\pi} \frac{Z_{\gamma} Z_{\gamma}^{5/2}}{v_p q^2} \left[ Z_{\gamma}^2 + (k - q)^2 \right]. \]

Expression Eq. (2.5) is appropriate for describing dipole-like transitions which cause soft-collision electrons and two-body binary-encounter interactions by bare projectiles.

**Bethe Theory**

The doubly differential cross section for the ejection of an electron from a hydrogen-like atom, differential with respect to energy \( \epsilon \) and solid angle \( \Omega \), can be written as an integral over the triply-differential cross section (TDCS) (Landau and Lifschitz, 1958) as

\[ \frac{d^2 \sigma}{d\omega d\Omega} = \int_{q_{min}}^{\infty} \frac{d^3 \sigma}{dq d\omega d\Omega} dq \]

where \( q_{min} = \Delta E / v_p \) is minimum momentum transfer in terms of the energy transfer \( \Delta E \) and the projectile velocity \( v_p \). Atomic units are used except where otherwise stated. As discussed earlier, the cross section for electron emission can be considered...
to consist of dipole and binary contributions. Thus, $q_{\text{min}} < q < 2v_p$ and this range can be divided into two parts: one for the dipole contributions with $q_{\text{min}} \leq q \leq q_0$ and the other for binary type collisions with $q_0 \leq q \leq q_{\text{max}} (\approx 2v_p)$. With these approximations the integration over $q$ can be separated into two parts to give:

$$\frac{d^2\sigma}{d\epsilon d\Omega} = \int_{q_{\text{min}}}^{q_0} \frac{d^3\sigma}{dq dq d\Omega} dq + \int_{q_0}^{q_{\text{max}}} \frac{d^3\sigma}{dq dq d\Omega} dq$$  \hspace{1cm} (2.8)

where the momentum $q_0$ is restricted within the range $q_{\text{min}} < q_0 < k$ and $k = \sqrt{2\epsilon}$ is the outgoing electron momentum. Furthermore, $q_0$ is chosen in such a way that the dipole term dominates throughout the low momentum transfer region.

Following the work by Bethe, Eq. 2.8 demonstrates the separation of the cross section into dipole and binary regions as shown in figure 2.2. In this figure, the TDCSs for the emission of an electron with momentum 2.7 a.u (corresponding to $\epsilon = 100$ eV) from atomic H by 3 MeV H\(^+\) impact are calculated analytically (Landau and Lifschitz, 1958) for the observation angles 30° and 90° as indicated. The dipole and binary regions can be separated reasonably at $q_0 \approx 1.6$ a.u. for 30°. For 90°, this separation is chosen arbitrarily, however. Since the dipole and binary transitions are associated with angular momenta changes $\Delta l = 1$ and $\Delta l \neq 1$, respectively, this separation becomes more reliable depending on the angular momentum transferred as discussed by Stolterfoht (Stolterfoht et al., 1998).

The figure shows that the angular distribution of fast ejected electrons exhibits a prominent peak, referred to as the binary peak, which narrows in width (not shown) as the electron energy increases (Rudd, 1992). This binary encounter peak has a maximum at an electron energy $\epsilon_{BE} = 4T\cos^2\theta$ for $0 \leq \theta \leq 90^0$, where $\theta$ is the electron observation angle and $T = E_p/M_p$ is the projectile energy reduced by the projectile mass $M_p$. The actual shape of the binary peak is determined by the initial.
bound electron momentum distribution, i.e., the Compton profile. In figure 2.2, the
binary region displays a broad maximum which peaks at the momentum
\[ q_{\text{bin}} = |\vec{k} - \vec{q}_i| \approx k, \]
where \( \vec{q}_i \) is the initial momentum of the bound electron.

\[ \text{3 MeV H}^+ \text{ on H} \]

\[ q_{\text{min}} \quad q_0 \quad q_{\text{bin}} \]

\[ \varepsilon = 100 \text{ eV} \ (k = 2.7 \text{ a.u.}) \]

\[ 90^\circ \quad 30^\circ \]

Dipole

Binary

Figure 2.2: Triply-differential cross sections (TDCS) with respect to momentum
transfer \( q \), energy \( \varepsilon \), and solid angle \( \Omega \) of the ejected electron (Landau and Lifschitz,
1958) as a function of \( q \) demonstrating the dipole and binary regions for the emission
of 100 eV electrons by 3 MeV H\(^+\) impact on atomic H. The momentum \( q_0 \approx 1.6 \text{ a.u.} \)
separates these regions for the electron observation angle of 30\(^\circ\) and is arbitrarily
chosen for 90\(^\circ\) (see text).
Figure 2.2 shows that the contributions of the dipole and binary parts depend strongly on the ejected electron angle. For example, at 30° the dipole contribution is larger than the binary part, while for 90° binary processes account for nearly all of the electron emission. Furthermore, the dipole contribution is greatly enhanced as $q_{\text{min}} \to 0$, i.e., for higher projectile velocities (not shown). So, it is clear from the figure that the influence of different ionization mechanisms changes significantly with electron emission angle.

**Electron Interference**

As already noted in the Introduction, a unique feature of collisions involving molecules is the presence of multiple atomic centers. By probing molecules with ions or photons possesses quite different from those observed for atoms can occur solely due to the existence of these multiple centers. Thus, the molecular structure is expected to play a prime role in determining the dynamics of electrons emitted from the multiple-center field. In particular, ionization from identical atomic centers by charged particles or photons gives rise to the possibility for interference effects. Thus, collisional dynamics can be used to probe the characteristics of these interferences.

The overall ionization of H$_2$, the simplest molecule composed of two identical centers, is well understood. However, phenomena associated specifically with the identical centers have not been explored. Because of this indistinguishability, the contributions to ionization from each center add coherently and interference effects might be expected in the ionization spectra. This phenomenon is analogous to Young’s two-slit experiment for light where both slits simultaneously emit radial waves giving rise to a diffraction pattern. In the following, electron interferences are analyzed using both quantum-mechanical and wave optics methods. Moreover, the
second-order interferences that result when the electron wave emitted at one center interferes with the same wave after it is backscattered at the other center, are deduced quantum mechanically as well as from phase differences using methods known from wave optics.

First-order Interference

First, consider the projectile-electron interaction for a bare nucleus (in our case H⁺) of charge $Z_p$ interacting with a molecular hydrogen target. The coordinates are defined in Fig. 2.3 with $\vec{d}$ the internuclear vector and $\vec{R}$ and $\vec{r}$ the position vectors of the projectile and the electron to be ionized, respectively. Interference effects in the electron emission from $\text{H}_2$ derive from the initial two-center wave function $\phi_i$ which can be expressed (Briggs et al., 2001, Galassi et al., 2002, Stolterfoht and Sulik, 2004) as

$$
\phi_i = \frac{1}{\sqrt{2N}} (\phi_{is}(\vec{r} + \vec{d}/2) + \phi_{is}(\vec{r} - \vec{d}/2)), \tag{2.9}
$$

where $\phi_{is}$ is the atomic 1s wave function centered at the two H atoms and $N < 1$ is an appropriate normalization factor. The final state is approximated by a plane wave (or a Coulomb distorted wave) centered at the origin located at the center of mass of the $\text{H}_2$ molecule.

In the Born approximation the cross section for ion induced electron emission from $\text{H}_2$, differential in the momentum transfer $\vec{q}$ and direction given by the solid angle $\Omega_q = (\theta_q, \phi_q)$ with polar angle $\theta_q$ and azimuthal angle $\phi_q$, ionized electron energy $\varepsilon$ and solid angle $\Omega$ and momentum $\vec{k}$ for the outgoing electron, can be
Figure 2.3: Coordinates for a projectile $Z_p$ interacting with an electron on molecular hydrogen (centers a and b).

expressed as (Briggs et al., 2001, Stolterfoht et al., 2001, Stolterfoht and Sulik, 2004):

$$\frac{d^4\sigma_{2H}}{dq d\Omega_q d\alpha d\Omega} = \frac{d^4\sigma_{2H}}{dq d\Omega_q d\alpha d\Omega} \left[ 1 + \cos (\vec{p} \cdot \vec{d}) \right]. \quad 2.10$$

The cross section $d^4\sigma_{2H}/dq d\Omega_q d\alpha d\Omega$ describes incoherent electron emission from the two H atoms (denoted by $2H$) acting independently. The interference is expressed by the term $\left[ 1 + \cos (\vec{p} \cdot \vec{d}) \right]$ caused by the two centers, where $\vec{p} = \vec{k} - \vec{q}$.

Furthermore, assuming that the relative position ($\vec{d}$) of the nuclei in the diatomic molecule remains fixed throughout the collision, the differential cross sections must be averaged over the random orientations of the internuclear $H_2$ axis. From Eq. (2.10), this averaging gives after dividing by $4\pi$,
The presence of the sine term, a damped Bessel function \(1 + \sin(pd)/pd\), shows that this averaging preserves the oscillatory features of the electron emission spectra (Stolterfoht et al., 2001, 2003).

To obtain the relevant cross sections to compare with experiment, in which the momentum transfer is not measured, Eq. 2.11 has to be integrated with respect to the momentum transfer \(q\):

\[
\frac{d^4\sigma_{2H}}{dqd\Omega_q dqd\Omega} = \frac{d^4\sigma_{2H}}{dqd\Omega_q dqd\Omega} \left[1 + \frac{\sin(pd)}{pd}\right] d\phi dq.
\]

Similar expressions have been derived for elastic electron scattering (A. Messiah, 1970), ionization by photons (Cohen and Fano, 1966), electrons (W. J. Moore 1955, Stia et al., 2003), and heavy ions (J.S. Briggs 2001, Galassi et al. 2002). To compare with experiment, the right hand side of Eq. (2.12) must be integrated over the momentum transfer \(q\) and the corresponding solid angle \(\Omega_q\).

To evaluate \(p = |\vec{k} - \vec{q}|\), we note from Fig. 2.4 that

\[
\cos \alpha_{\vec{k}q} = \cos \theta \cos \theta_q + \sin \theta \sin \theta_q \cos \phi_q
\]

where \(\vec{K}_i\) and \(\vec{K}_f\) are initial and final momenta of the projectile, respectively, with \(\vec{q} = \vec{K}_i - \vec{K}_f\), \(\theta\) is the angle between \(\vec{k}\) and \(\vec{K}_i\), and \(\alpha_{\vec{k}q}\) is angle between \(\vec{k}\) and \(\vec{q}\). The polar angle \(\theta_q\) is fixed due to the relations \(\cos \theta_q = q_/q = q_{\text{min}}/q\) and \(\sin \theta_q = q_\perp/q = \sqrt{q^2 - q_{\text{min}}^2}/q\) where \(q_\perp\) is the component of \(\vec{q}\) perpendicular to \(\vec{K}_i\). Combining these relations we obtain

\[
p = \left[q^2 + k^2 - 2k \left(q_{\text{min}} \cos \theta + \sqrt{q^2 - q_{\text{min}}^2} \sin \theta \cos \phi_q\right)\right]^{1/2}.
\]
As discussed earlier, in accordance with Bethe's approximation the cross section for electron emission can be considered to consist of so-called dipole and binary contributions. It has been recognized (Stolterfoht et al., 1998) that photon-like dipole transitions (\( \Delta l = 1 \)) for which \( q \approx 0 \) and binary encounter interactions (\( \Delta l \neq 1 \)) between the projectile and the emitted electron play essentially different roles in the ionization process. The dipole part has a sharp maximum at the minimum momentum transfer \( q_{\text{min}} = \Delta E / v_p \), where \( \Delta E \) is the energy transferred in the collision and \( v_p \) is the projectile velocity. Then, for the dipole part of Eq. (2.12) \( p \) can be approximated by \( p = k - q_{\text{min}} \). On the other hand, binary interactions involve essentially only the projectile and the target electron so that \( q = k - p_i \approx k \) where \( p_i (<< k) \) is the mean initial momentum of the bound electron, and, therefore, \( p \sim 0 \). With these approximations the integration over \( q \) can be carried out separately for the dipole and binary parts in Eq. (2.10) to give:
where $s = 1 + \sin(p_d d)/p_d d$ with $p_d \approx 1$ a.u. is a constant. Thus, from Eq. 2.15a it is obvious that the oscillatory interference behavior is governed by the dipole part with the binary part contributing only a constant term. Furthermore, these oscillatory structures in the cross section are expected to be enhanced for high collision velocities and relatively small ejection angles where dipole transitions dominate (see Fig. 2.2). For very high projectile velocities, the argument of the sine function becomes simply $kd$ predicting one full sinusoidal oscillation of the interference structure in the range $kd = 0-2\pi$. For the H$_2$ internuclear distance of 1.42 a.u., this result indicates an interference structure that goes through one full oscillation for $k = 0-4.4$ a.u., corresponding to emitted electron energies $\varepsilon$ ranging from about 0-250 eV ($k = \sqrt{2\varepsilon}$). Furthermore, except for a variation in the magnitude of the interference due to the relative contributions of the dipole and binary parts, Eq. (2.15a) predicts that the oscillatory interference structure should be independent of the electron emission angle.

In theoretical work by Nagy (Nagy et al., 2002), an extended treatment of the interference term in Eq. (2.12) was formulated using a semi-classical impact-parameter model for molecular targets based on the Born approximation and expressed as

$$\frac{d^2 \sigma_{H_2}}{d\Omega d\varepsilon} = \frac{d^2 \sigma_{\text{dip}}}{d\Omega d\varepsilon} \left[ 1 + \frac{\sin(kd)}{kd} \right] + \frac{d^2 \sigma_{\text{bin}}}{d\Omega d\varepsilon} s$$

where $s = 1 + \sin(p_d d)/p_d d$ with $p_d \approx 1$ a.u. is a constant. Thus, from Eq. 2.15a it is obvious that the oscillatory interference behavior is governed by the dipole part with the binary part contributing only a constant term. Furthermore, these oscillatory structures in the cross section are expected to be enhanced for high collision velocities and relatively small ejection angles where dipole transitions dominate (see Fig. 2.2). For very high projectile velocities, the argument of the sine function becomes simply $kd$ predicting one full sinusoidal oscillation of the interference structure in the range $kd = 0-2\pi$. For the H$_2$ internuclear distance of 1.42 a.u., this result indicates an interference structure that goes through one full oscillation for $k = 0-4.4$ a.u., corresponding to emitted electron energies $\varepsilon$ ranging from about 0-250 eV ($k = \sqrt{2\varepsilon}$). Furthermore, except for a variation in the magnitude of the interference due to the relative contributions of the dipole and binary parts, Eq. (2.15a) predicts that the oscillatory interference structure should be independent of the electron emission angle.

In theoretical work by Nagy (Nagy et al., 2002), an extended treatment of the interference term in Eq. (2.12) was formulated using a semi-classical impact-parameter model for molecular targets based on the Born approximation and expressed as

$$\frac{d^2 \sigma_{H_2}}{d\Omega d\varepsilon} = \frac{d^2 \sigma_{\text{dip}}}{d\Omega d\varepsilon} \left[ 1 + \frac{\sin[(k_\parallel - q_{\min})d]}{(k_\parallel - q_{\min})d} \right] + \frac{d\sigma_{\text{non}}}{d\Omega d\varepsilon} s$$

In this model it was found that $k$ should be replaced by $k_\parallel = k\cos\theta$ ($\theta$ is the electron observation angle), i.e., the electron momentum component parallel to the ion beam (see Fig. 2.4). The dipole and binary parts of the cross section in Eq.
(2.15a) then become instead the interfering and non-interfering contributions to the cross section, respectively. For the 1-5 MeV ($v_p \approx 6.4-14$ a.u.) H$^+$ projectiles used in the present work, $q_{\text{min}}$ is not negligible and is expected to have a noticeable effect on the interference structure, in contrast to the work of Stolterfoht et al. (Stolterfoht, 2001, 2003, 2004) for which $q_{\text{min}}$ could be neglected due to the high projectile velocity. For high velocity collisions $q_{\text{min}}$ is small, and, accordingly, Eq. (2.15b) predicts the frequency of the oscillatory structure to vary approximately with $\cos \theta$.

Also, it is noted that numerical integration of Eq. (2.12) using cross sections $d^3\sigma_{2H}/dqdlde$ for independent H atoms obtained from the Born approximation (as discussed earlier) leads to a varying oscillation frequency due to the integration over $q$ as will be shown in chapter 5 (Results and Discussions).

First-order Interference: Wave Optics Approach

Interference phenomena can also be derived from the methods of wave optics, in which the first-order interference that is analogous to Young's experiment can be obtained from the phase differences (Stolterfoht et al., 2004). First, consider the electromagnetic wave represented by the Born operator $e^{iq \cdot \ell}$ with momentum transfer $\vec{q}$ incident on two H centers labeled a and b as shown in Fig. 2.5. This wave produces plane waves of momentum $\vec{k}$ with the first-order amplitudes $A_a$ and $A_b$ at each of the centers a and b, respectively.

Since the amplitudes are the same for these identical atomic centers ($A = |A_a| = |A_b|$), the intensity at a given electron observation angle is $I = 2|A|^2[1+\cos \delta]$, where $\delta$ is the relative phase between the amplitudes. Now, $\delta = \delta_k - \delta_q$, where $\delta_q$ and $\delta_k$ are created along the paths crossing the centers a and b, respectively. Using the relations, $\delta_q = qdcos \alpha_q = \vec{q} \cdot \vec{d}$ and $\delta_k = kdcos \alpha_k = \vec{k} \cdot \vec{d}$, we obtain following expression

20
Equation 2.16 can be compared with Eq. (2.10) showing that these equations are identical by replacing $\bar{p} = \vec{k} - \vec{q}$ and $2|A|^2 = d^2\sigma_{2\Pi}/d\vec{q}d\Omega \cdot d\vec{d}d\Omega$.

Figure 2.5: First-order interference deduced from wave optics for the incident plane wave of momentum transfer $\vec{q}$ giving rise to the simultaneous emission of outgoing waves of momentum $\vec{k}$ denoted by the amplitudes $A_a$ and $A_b$ (Stolterfoht et al. 2004).

Second-order Interference

The second-order oscillatory effects are attributed to interference of the primary ejected electron wave with the secondary wave that results from scattering at the other atomic center, an effect that has no analogy in Young’s two-slit experiment (Stolterfoht et al., 2004). This rescattering phenomenon is totally different from Young’s two-slit experiment, where both slits simultaneously emit radial waves.
Then, the second-order interference can be expressed by the superposition of two paths with the first and second order amplitudes \( A_{f} \) and \( B_{f} \), respectively (Stolterfoht and Sulik, 2004). Hence, the cross section for \( \text{H}_2 \) can be written as:

\[
\frac{d^4 \sigma_{\text{H}_2}}{dq d\Omega q d\omega d\Omega} = \frac{4kZ_p^2}{v_p q^3} \left| A_f + B_f \right|^2.
\]  \hspace{1cm} 2.17

The first order amplitude is expressed as

\[
A_f(q) = \langle \varphi_k | e^{i\vec{q} \cdot \vec{r}} | \varphi_o \rangle
\]

where \( \varphi_o \) is the atomic wave function and the final state \( \varphi_k \) is a plane wave or a Coulomb distorted wave (Salin, 1969; Inokuti, 1971).

The second-order amplitude is given by (Stolterfoht and Sulik, 2004)

\[
B_f = \frac{1}{2\pi d} \langle \varphi_k | V_c | \varphi_k \rangle \langle \varphi_k | e^{i\vec{q} \cdot \vec{r}} | \varphi_o \rangle,
\]

where \( \varphi_k \) is a Coulomb wave propagating along the internuclear vector \( \vec{d} \) and \( V_c \) is the Coulomb potential representing the elastic interaction of an electron with an \( \text{H} \) atom. After algebraic manipulation, the cross section of Eq. (2.17) is given by

\[
\frac{d^4 \sigma_{\text{H}_2}}{dq d\Omega q d\omega d\Omega} = \frac{4kZ_p^2}{v_p q^3} \left[ \left| A_f \right|^2 + \left| B_f \right|^2 + 2 \text{Re} \left( A_f B_f^* \right) \right],
\]  \hspace{1cm} 2.20

where the third term represents the interference of the first- and second-order amplitudes.

It is noted that the matrix elements are complex and depend on the orientation of the molecule. Due to the complexity of these matrix elements, Eq. (2.20) was not evaluated (Stolterfoht and Sulik, 2004). However, the second-order formalism will be explained further in the next section using the wave optics methods.
Second-order Interference: Wave Optics Approach

To understand the physical origin of the second-order interference, consider the phase diagram illustrated in Fig. 2.6. The figure displays the ionization at one center $a$ by the incident wave which is rescattered at the second center $b$. The incident wave of momentum $\vec{q}$ is split at center $a$ into a direct path with amplitude $A_a$ and a backscattered path, propagated along the internuclear separation vector $\vec{d}$ and then scattered at $b$, with amplitude $B_a$ associated with the outgoing momentum $\vec{k}$. Then, the second-order interference is due to the phase difference $\delta = \delta_k - \delta_d$, where the phase $\delta_d = kd$ is created when the wave propagates from one center to the other, and the intensity for branch $a$ can be expressed as (Stolterfoht and Sulik, 2004),

$$I_a^2 = |A_a|^2 + 2|A_a B_a| \cos(k \cdot \vec{d} - kd).$$  \hspace{1cm} 2.21

Assuming, $A_a$ and $B_a$ to be constant (for simplicity only, not correct in reality), then Eq. 2.21 may be averaged over the random orientation of $\vec{d}$ and divided by $4\pi$ to obtain a qualitative understanding of the oscillation frequency produced in the second-order interference according to the relation (Stolterfoht et al., 2004):

$$\bar{I}_a^2 = |A_a|^2 + 2|A_a B_a| \frac{\sin(2kd)}{kd}.$$  \hspace{1cm} 2.22

This expression predicts that the frequency of the oscillation is doubled as the electron wave propagates from one center to the other. According to Stolterfoht [Stolterfoht et al., 2004], the doubling effect is independent of the electron emission angle.

Now, considering the other branch $b$, i.e., including also the primary emission from the second center, additional waves with amplitudes $A_b$ and $B_b$ should appear in the second order intensity calculation, which can then expressed as:
Integrating over the molecular orientation again assuming the $A_a$'s and $B_a$'s are constant and combining Eqs. (2.21) and (2.23), the final form of the second-order interference with rescattering can be written as (Stolterfoht et al., 2004),

$$I_2 = \bar{I}_1 + 2|A_a| |B_a| \left[ \frac{\sin(2kd)}{kd} + 2 \frac{\cos(kd) \sin(qd)}{qd} \right]$$

where the sum of the terms inside the bracket appears as an oscillatory structure superimposed on the first-order interference $\bar{I}_1$.

Figure 2.6: Schematic showing interference of the primary ejected electron wave of amplitude $A_a$ from center a with the secondary wave of amplitude $B_a$ that results from scattering at the other atomic center b.
Again, the first term in the bracket points to a doubling of the second-order interference structure as in the case of Eq. (2.22), with an additional term that varies depending on the type of collision process, i.e., dipole- \( q \approx 0 \) or binary encounter \( (q \approx k) \) (Stolterfoht et al. 2004). For forward angles, dipole transitions \( (q \approx 0) \) dominate so this second term has the same frequency as the first-order interference (Eq. 2.15b). On the other hand, for binary encounter collisions with \( q \approx k \), the second term is also doubled in the oscillation frequency and can be added directly to the first term. However, it is emphasized that these equations describing the second-order interference may not accurately represent the observed behavior due to the approximations required to carry out the integrations.
EXPERIMENTAL PROCEDURE

Ion Source and Accelerator

The measurements were performed at Western Michigan University using the 6-MV tandem Van de Graaff accelerator (Figure 3.1) where positive charge is delivered to the high voltage terminal by a recently installed (2003) Pelletron charging system consisting of a chain of metal and nylon links. Since this accelerator is a tandem, a proton beam can be accelerated to twice the terminal voltage, i.e., up to 12 MeV. This accelerator facility has two negative ion sources: a SNICS (Source of Negative Ions by Cesium Sputtering) and a direct extraction negative ion exchange source. The exchange ion source, which makes negative ions from gases, was used to produce beams of H\(^+\) ions for the work described here.

Scattering Chamber and Gas Target

Beams of 1, 3, and 5 MeV H\(^+\) of intensity 0.1 – 0.5 \(\mu\)A were directed into the scattering chamber located in the rightmost beam line of Figure 3.1. The details of the scattering chamber are shown in Fig. 3.2. Considerable care was taken to reduce beam-induced background electrons by collimating the beam. First, the ion beam was collimated by a 4-jaw (4mm×4mm) aperture system, \(A_1\), prior to entering the scattering chamber, and was further collimated by two circular apertures (\(A_2\), \(A_3\)) placed just inside the chamber. These latter apertures were 2.5 cm apart with diameters of 3.5 mm and 4.0 mm for \(A_2\) and \(A_3\), respectively. The apertures were positively biased (+300V) to prevent the escape of secondary electrons into the
chamber. A grounded shield (S), large enough to let the main beam pass but small enough to stop most scattered particles (ions and electrons) (diameter = 1 cm), was installed just downstream (about 1 cm) of aperture A₃ to prevent the electric field of the biased apertures from penetrating into the collision region.

The target gas was supplied by a jet of diameter ~ 2 mm, with the flow rate set to maintain a pressure of not more than a few times 10⁻⁵ Torr throughout the scattering chamber. The target gas pressure was varied and the electron yield measured to ensure that single-collision conditions prevailed in the interaction region. The gas flow rate into the chamber was monitored by a capacitance manometer.

Figure 3.1: Schematic drawing of the Western Michigan University tandem Van de Graaff Accelerator and associated beam lines (S. M. Ferguson 2004).
connected to a feedback control system so that the chamber pressure remained at a predetermined fixed value during the measurements. The base pressure (with the jet off) in the scattering chamber was $< 1 \times 10^{-6}$ Torr and was achieved using a diffusion pump.

The gas jet was movable vertically relative to the scattering plane defined by the ion beam and the electron trajectory and must be properly aligned even for relative measurements. The tip of the jet was normally adjusted to a height of 3.5 mm above the axis of the proton beam as discussed below.

![Figure 3.2: Schematic of scattering chamber (not to scale) and the collision region for making differential cross section measurements of electron emission. $A_1$ is the 4-jaw collimator located prior to the scattering chamber, $A_2$ and $A_3$ are circular apertures respectively, $S$ a grounded shield, $SC$ the scattering center, $FC$ the Faraday cup, $FCS$ the Faraday cup suppressor, AES the angular electron spectrometer, and CEM the channel electron multiplier.](image-url)
A parallel-plate angular electron spectrometer (AES) equipped with a channel
electron multiplier (CEM) was used to detect ejected electrons in the energy range
\(\sim 3-300\) eV at observation angles \(30^\circ, 60^\circ, 90^\circ, 120^\circ,\) and \(150^\circ\) relative to the incident
proton beam direction. Beam induced electron background was determined by taking
spectra without the target gas. Magnetic fields inside the scattering chamber were
minimized by shielding with a \(\mu\)-metal liner. The incident beam intensity was counted
downstream in a tantalum Faraday cup (FC), which was suppressed to -200V to
prevent the escape of backscattered electrons. However, the sputtering yield for
protons is less than 1\% for most materials (Thomas, 1985), so that backscattered
electrons from the Faraday cup was not a serious problem.

Data Acquisition and Spectrometer Control

A LABVIEW data acquisition program, developed by S. Rumega (M.A.
Thesis, 2000), was used to control the voltages applied to the spectrometer and to
acquire the measured spectra. Electron counts corresponding to electron energy were
recorded by this program. Processing of the detected electron signals and supplying
the spectrometer voltages were carried out using the electronics shown in figure 3.3.
An electron analyzed by the angular spectrometer is detected by a channeltron (see
below). The channeltron signals were sent to a fast timing amplifier (FTA) that gave
an output signal of \(\sim 2-3\) V. These amplified signals were then transmitted to a
constant fraction discriminator (CFD) to eliminate noise and background signals by
setting a threshold voltage. By stopping the projectile beam upstream of the
scattering chamber, electronic noise was identified. However, these signals were
observed to have a negligible amplitude compared to the true electron signals. Then
Figure 3.3: Block diagram of the supporting electronics for spectrometer control and data acquisition.
the discriminated electron signals were sent to a CAMAC (Computer Automated Measurement And Control) scalar to be counted. The data acquisition portion of the LABVIEW program recorded the number of counts corresponding to each electron energy for a preset energy range by stepping the voltages on the plates of the spectrometer and displaying the results graphically on the monitor.

The electron counts at each energy were normalized to the projectile beam intensity as collected in the Faraday cup at the end of the beamline. A Keithley electrometer measured the current in the Faraday cup. The full scale current from the electrometer gives a 2 V dc output, which was dropped across a 1 MΩ resistor to convert the voltage output to a current output. Then a digital current integrator (DCI) converted this current into logic pulses which were counted by the CAMAC scalar. In this way, the electron energy is stepped in small intervals from a starting value to an ending value thereby completing one scan and creating an electron spectrum. The program has the option to acquire multiple scans over the energy range to obtain better statistics.

Angular Electron Spectrometer

A rotatable electron spectrometer for measuring electron spectra was mounted in the collision chamber. This system can detect and analyze the energy of continuum electrons emitted within a range of about 20° – 160° with respect to the beam direction. A schematic is shown in figure 3.4. The spectrometer consists of a 45° plane-mirror analyzer (D. Roy and D. Tremblay, 1990) that acts as a capacitor and deflects electrons with a given energy into the channel electron multiplier (CEM). The term “channeltron” will be used for further reference below.
Figure 3.4: Schematic diagram of the parallel-plate angular electron spectrometer. The H\textsuperscript{+} beam travels out of the page.

The electron charge $e$, passage energy $E$, and the potential difference $\Delta V$ between the parallel plates are related by the geometric factor of the spectrometer, known as the spectrometer constant $k$:

$$E_0 = \frac{e\Delta V}{k} \quad \text{(3.1)}$$

For $45^\circ$ analyzers, the spectrometer constant can be calculated using the following relation (Woitke, 1996),

$$k = \frac{Z_0}{2l} \quad \text{(3.2)}$$
where \( Z_0 \) is the distance between the entrance and the exit slits and \( l \) is the plate separation as shown in figure 3.5.

![Electron trajectory diagram for a parallel-plate spectrometer](image)

Figure 3.5: Electron trajectory diagram for a parallel-plate spectrometer (see text).

The energy spread of the transmitted electrons, i.e., the energy resolution \( \Delta E \), is given by the relation

\[
R = \frac{\Delta E}{E_0} = \frac{2\Delta S}{Z_0},
\]

where \( \Delta S \) is the width of the entrance and exit slits (Harrower, 1955) and \( R \) is the constant intrinsic instrumental resolution (D. Roy and D. Tremblay, 1990). For the angular electron spectrometer used in the present measurement \( R \approx 3\% \).
The spectrometer can be operated in three possible modes depending on the desired resolution: (1) low resolution, (2) high resolution, constant outgoing electron energy, and, (3) high resolution, constant electron deceleration. Additionally, each of these modes can be used for high or low analyzing energies. For this experiment, the spectrometer was operated in the low resolution mode with high analyzing energies using a voltage divider (see below) to obtain electron energies in the range of 3-300 eV. The voltage divider decreased the power supply voltage by a nominal factor of 10 to obtain the desired range. Since a full sinusoidal oscillation is expected in the

![Parallel-plate electron spectrometer](image)

Figure 3.6: Parallel-plate electron spectrometer in low-resolution, high-energy mode. E is the electron energy to be analyzed and k is the spectrometer constant. The voltage on the black plate, V_B, deflects electrons of energy E=\(eV/k\) entering the spectrometer by 90°. The grid voltage V_G is the same as V_B.
range ~ 0 - 4.4 a.u. (as discussed above in chapter 2) in the present work, it is sufficient to measure the ionization of H\textsubscript{2} by using the spectrometer in low resolution mode. A schematic diagram for the basic setup is shown in figure 3.6. The required voltage that must be applied to the parallel plates is given by \( V_B = -kE \), where \( k \) is the spectrometer constant and \( E \) is the energy of the incoming electron.

The bias voltage \( V_G \) applied to a grid that was placed just beyond the exit slit (in front of the CEM housing) had the same voltage as the back plate, \( V_B \) was used to suppress spurious low-energy electrons (it repels electrons with energies less than \( kE \)) and to allow higher energy electrons to pass.

The spectrometer is connected to a stepping motor system to control the angular setting. This mechanical gear system translates one full motor rotation to a 2° spectrometer rotation (Woitke, 1996). In order to be able to track the rotations and determine the absolute position of the motor, the spectrometer is connected to an encoder that sends the position and information to the spectrometer control program.

Electron Detector

After being analyzed by the spectrometer an electron energy spectrum is obtained by scanning a given energy range (using the control PC) and counting the number of pulses originating from the electrons striking the channeltron at each energy normalized to the incident beam intensity. The principle and operation of the channeltron is described in Burle Electro-optics Inc. Handbook (Burle Inc., 2002 and references therein). The channeltron, model 4821G with a gain of \( 1.0 \times 10^8 \), was used for the electron measurements in this work. The channeltron has an efficiency that depends on the energy of the emitted electrons as shown in figure 3.7 (from Burle handbook). The CEM required an operating voltage of about +2400V and this was...
accomplished by biasing the base to a voltage of \(~+2600\text{V}\) and the cone to \(+200\text{ V}\) (see Fig. 3.4). By biasing the cone prior to electrons striking the multiplier helps to achieve a relatively constant CEM detector efficiency over the energy range of the ejected electrons (see Fig. 3.7). Dark counts, i.e., counts that occur without any true electron detection, have been observed to occur with a rate less than \(0.1/\text{sec}\).

![Graph showing channeltron electron detection efficiency as a function of electron energy (eV).](image)

**Figure 3.7:** Typical channeltron electron detection efficiency as a function of electron energy (eV) (Burle, Channeltron Handbook, 2002).

**Nozzle Position**

To determine the best vertical position for the jet, measurements were taken by placing the tip of the target gas nozzle at different heights from the proton beam axis. Figure 3.8 shows the variations of the count rate with the nozzle position by the
impact of 3 MeV H\(^+\) on H\(_2\) at 90° observation angle. When the nozzle position was half a turn up (1 turn = 1.25 mm) relative to the beam axis, it produced a shower of background electrons sputtered from the nozzle by the edges of the projectile beam. By raising the tip of the nozzle gradually, a clear change in the count rate was observed. After a certain nozzle height, the count rate became nearly constant and the nozzle position was set to this value, which was 3.5 mm above the beam axis.

![Figure 3.8: Background electron counts as a function of nozzle position above the beam axis (1 turn = 1.25 mm). Data are for 3 MeV H\(^+\) on H\(_2\) at 90°.](image)

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Calibration of Voltage Divider

The power supply used in the experiment has the limitation that it normally operates only above 50V. Thus, a 10:1 voltage divider was used at the output of the supply to obtain the low voltages required to be applied to the spectrometer plates. In order to calibrate the voltage divider corresponding to electron energies in the range 1-300 eV, measurements were taken for the ionization of He using a 1 MeV H\(^+\) beam for which KLL Auger emission is known to occur at 33 eV (Stolterfoht, 1987). This Auger peak is shown in Fig. 3.9 for 1 MeV H\(^+\) on He at 90\(^\circ\) observation angle. If, however, with the voltage divider factor set to 10 by the LABVIEW program, the Auger electron peak is displaced from its actual value, the division factor can be set to a value that places the Auger peak at the correct value of 33 eV. The actual division factor was found to be 10.5.

![Figure 3.9: Electron emission from He showing a distinct Auger peak near 33 eV.](image.png)
The voltage divider was also tested by measuring the cusp electron energy, which is characterized by the reduced energy $T = (m/M)E_p$, where $(m/M)$ is the electron-projectile mass ratio, and $E_p$ is the energy of the projectile ion. These cusp electrons, which travel along the beam direction with the velocity of the beam, produce a large peak in the electron spectrum (see for example, Gulyas et al., 1992), so the position of this peak can be used as a check on the value found for the voltage division factor. For 1 MeV H$^+$ the cusp is expected to appear at $1 \text{ MeV}/1836 = 545$ eV, where the electron-projectile mass ratio is 1836. Using this projectile energy for H$^+$ ions on He at 90° observation angle, the cusp electron energy was measured (using the division factor of 10.5) with and without using the voltage divider. In both cases, the cusp was found to have almost identical energies which were close to 545 eV, thereby providing a check on the voltage divider factor.
DATA ANALYSIS

Measurements of the cross sections were carried out for the electron energy range 3-300 eV and observation angles 30°, 60°, 90°, and 150° relative to the incident beam direction for impact energies 1, 3, and 5 MeV for H⁺ on H₂. The target hydrogen gas in the scattering chamber was kept at a constant pressure of 5×10⁻⁵ Torr. Figure 4.1 shows some typical results for the extreme electron emission angles of 30° and 150°. At 30° the background counting rate was about 10% of that with H₂ in the scattering chamber; on the other hand, at 150° the background rate was about 25% of the counting rate for H₂. The background (no gas) curve has a similar shape.

Figure 4.1: Typical experimental data for 1 MeV H⁺ on H₂ at 30° and 150° observation angles.
to that for H₂, except at the lowest energies, and was quite reproducible showing only small changes from day to day. However, larger uncertainties are expected at energies smaller than ~5 eV where the electron count rate can be affected by spurious instrumental effects (for e.g., secondary electrons from surfaces within the target region struck by scattered beam ions). At high electron energies, especially at 150°, the data are less accurate above 100 eV, since they are increasingly influenced by limited statistics and the underlying background (see Fig. 4.1).

Several plots were made of the number of counts as a function of the target gas pressure, resulting in straight lines to within the counting statistics. This result showed that the increase in number of counts is directly proportional to the increase in pressure of target hydrogen gas, and demonstrated the absence of multiple collisions. Figure 4.2 shows the pressure dependence of the autoionization electron

Figure 4.2: Target gas pressure (in the scattering chamber) dependence of the autoionization electron production (at ~13 eV) for 3 MeV H⁺ on H₂. The linear dependence of the electron yield on the target pressure indicates that single collision conditions are satisfied up to at least 40 mTorr.
(at ~13 eV) yield at 90° for 3 MeV H\(^+\) on H\(_2\) collisions. This result indicates that single collision conditions exist up to at least 40 mT. The same procedure was used for each projectile energy to ensure the single collision conditions prevailed in every collision systems.

To verify the reliability of the H\(_2\) data, and to provide a benchmark for interference features, additional measurements were conducted for the ionization of He by the same projectiles to show that the experimental data are well reproduced by theoretical calculations. This allows a comparison for monatomic and diatomic targets to show that no interference effects exist for monatomic species. The same procedure was followed in previous work (Stolterfoht, 2001, 2003, Hossain, 2003).

Experimental and theoretical results for electron emission from H\(_2\) and He at the angles 30°, 60°, 90° and 150° (relative to the beam direction) for the projectile energy 3 MeV H\(^+\) are shown in the upper panels of Figs. 4.3-4.6. The cross sections are seen to decrease by several orders of magnitude for ejected electron energies in the range 5-250 eV. In order to reveal interference effects, which vary only by at most a factor of two (see Eq. 2.12), the molecular cross sections were normalized to theoretical atomic cross sections using the Born (B1) approximation (Stolterfoht, 1997). Because we are dealing moderately high projectile velocities, the perturbation strength \(Z_P/v_P \ll 1\) (\(Z_P\) is the atomic number of the projectile and \(v_P\) is the projectile velocity in a.u.), two-center effects between the projectile and the target are expected to be small (Stolterfoht, 1997). So it is justified to use the Born approximation given by Eq. (2.5) to calculate the theoretical cross sections for 2H. These Born results are found to agree well with the continuum distorted wave-eikonal initial state (CDW-EIS) calculation (Gulyas, 1995) as displayed in Fig. 4.7. For 30° and 150° emission angles in 3 MeV H\(^+\) on H\(_2\) collisions, the agreement is remarkably good, and at 90°
the Born approximation and the CDW-EIS calculations are essentially identical. The Born calculations for H were performed using an initial hydrogenic wave function with an effective target charge of $Z_t = 1.19$ as discussed in chapter 2.

The lower panels of Figs. 4.3-4.6 display the ratio of experimental to theoretical cross sections according to Eq. 5.2. As seen in the lower panels, the He data show a distinct peak near 33 eV (Stolterfoht, 1987) where KLL Auger emission occurs. Other than this Auger peak, the He data show a nearly monotonic behavior (except at 90°) with increasing electron energy. The overall ratio deviates from unity indicating an increasing disagreement between experiment and the theory. At the same time, for electron energies above ~125 eV, the experimental cross sections show large percentage of background (not shown), especially at 150° ejection angle.

On the other hand, the normalized cross section ratios for H₂ at 30° and 150° display clear non-monotonic behavior suggestive of oscillatory structures. For the observation angles 60° and 90° (see chapter 2 and 5), electron emission is increasingly affected by binary collisions, and, hence, oscillatory features become weaker as the emission angle increases up to 90° as shown in the lower panels of Figs. 4.4 and 4.5. All of these cross section ratios are well outside the experimental uncertainties of the relative cross sections, which are less than ± 5%. However, above ~ 125 eV the statistical error is larger than ± 5% (error increases with the increase of electron ejection energy, however, the statistical error is about ± 20% at 200 eV electron energy). Also, a reproducible peak due to autoionization (AI) is observed near 13 eV (Stolterfoht et al., 2003). The contribution of this autoionization peak was found to have a nearly negligible affect on the overall oscillatory behavior of the H₂ spectra (Stolterfoht et al., 2001).
Previously, the $H_2$ cross section ratios were calculated using an effective target charge of $Z_t = 1.05$ (Stolterfoht, 2001, Hossain, 2003) for the initial hydrogenic wave function instead of the value $Z_t = 1.19$ used here. With this $Z_t = 1.05$, however, the ratios show an overall increase with electron energy. Stolterfoht et al. (Stolterfoht, 2003), found that $Z_t = 1.19$, obtained from a variational treatment, is a better value for the effective charge of the $H_2$ target. Using this higher effective charge, the corrections to the cross sections ratios (a straight line fit was required to give an average experimental to theoretical ratio of unity) required in this earlier work (Stolterfoht et al., 2001, Hossain et al., 2003) were not needed.
Figure 4.3: Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 30° with respect to the incident beam direction. Upper panels: Measured and theoretical Born cross sections are compared for H₂ and He. For H₂, the theoretical cross sections represent ionization from the two H centers independently. Lower panels: Experimental to theoretical cross section ratios for H₂ and He. The arrows indicate the autoionization (AI) or Auger electrons (see text).
Figure 4.4: Cross sections for electron emission from H$_2$ and He by 3 MeV H$^+$ as a function of ejected electron energy at the observation angle of 60° with respect to the incident beam direction. Upper panels: Measured and theoretical Born cross sections are compared for H$_2$ and He. For H$_2$, the theoretical cross sections represent ionization from the two H centers independently. Lower panels: Experimental to theoretical cross section ratios for H$_2$ and He. The arrows indicate the autoionization (AI) or Auger electrons (see text).
Figure 4.5: Cross sections for electron emission from H₂ and He by 3 MeV H⁺ as a function of ejected electron energy at the observation angle of 90° with respect to the incident beam direction. Upper panels: Measured and theoretical Born cross sections are compared for H₂ and He. For H₂, the theoretical cross sections represent ionization from the two H centers independently. Lower panels: Experimental to theoretical cross section ratios for H₂ and He. The arrows indicate the autoionization (Al) or Auger electrons (see text).
Figure 4.6: Cross sections for electron emission from $\text{H}_2$ and He by 3 MeV $\text{H}^+$ as a function of ejected electron energy at the observation angle of 150° with respect to the incident beam direction. Upper panels: Measured and theoretical Born cross sections are compared for $\text{H}_2$ and He. For $\text{H}_2$, the theoretical cross sections represent ionization from the two H centers independently. Lower panels: Experimental to theoretical cross section ratios for $\text{H}_2$ and He. The arrows indicate the autoionization (Al) or Auger electrons (see text).
Figure 4.7: Theoretical double differential cross sections (DDCS) for electron emission at 30°, 90°, and 150° angles in 3 MeV H⁺ on H₂ collisions. The data are calculated using the Born approximation (Eq. 2.5) (solid lines) and the CDW-EIS theory (dotted lines).
RESULTS AND DISCUSSION

Overview

In this chapter, the experimental results on electron emission induced by 1, 3 and 5 MeV H\(^+\) ions impacting on H\(_2\) molecular targets will be presented and discussed. The data (such as those displayed in Figs. 4.2-4.5) exhibit oscillatory structures, attributed to first-order Young-type interference, superimposed on the exponentially decreasing cross sections for ionization. It will be shown that the oscillatory behavior exhibits a strong dependence on the electron observation angle and, additionally, a dependence on the collision velocity. These dependences are in qualitative agreement with the predictions of the Born approximation. The measured and calculated results are used to parameterize the changing frequency of the oscillatory structure as a function of the collision velocity. Higher-frequency oscillations superimposed on the primary (first-order) structure and attributed to interference of the primary ejected electron wave at one H center with the secondary wave produced following scattering at the other atomic center are also observed. These second-order oscillations exhibit only a small dependence on the electron observation angle with a frequency about three times higher than the first-order oscillations, and these oscillatory structures are independent of the collision velocity. Additionally, there is evidence for still higher frequency oscillations (about a factor of 20 higher than the primary structures) superimposed on the second-order oscillations. These oscillations appear to be independent of collision velocity and electron ejection angle. It is suggested that the origin of these latter oscillations is due to electron
emission from transient molecular formation with the incoming H\(^{+}\) ion. The details of each of these various structures are discussed in detail below.

**First-order Interference**

**Experimental Results**

In Fig. 5.1, the overall oscillatory interference features are displayed as a function of the ejected electron velocity (in atomic units) for electron observation angles 30°, 60°, 90° and 150° with respect to the incident beam direction for 1, 3 and 5 MeV H\(^{+}\) projectiles impacting on H\(_{2}\). In the figure, the measured doubly differential (in electron energy and observation angle) cross sections for electron emission from H\(_{2}\) have been divided by theoretical cross sections for the ionization of atomic hydrogen (times 2) as in earlier work (Stolterfoht et al., 2001, 2003). This normalization can be expressed as

\[
\left( \frac{d^2 \sigma_{H_2}}{d\Omega dE} \right)_{\text{norm}} = \left( \frac{d^2 \sigma_{H_2}}{d\Omega dE} \right)_{\text{exp}} / \left( \frac{d^2 \sigma_{2H}}{d\Omega dE} \right)_{\text{theo}}.
\]

This normalization procedure is necessary in order to reveal the interference features, which vary only by at most a factor of two, superimposed on the strongly decreasing cross sections (about four orders of magnitude) for electron emission over the energy range 3-300 eV. Because of limited statistics, the measured cross sections are less accurate for electron velocities (energies) greater than about 3 a.u. (~120 eV), while below ~ 0.5 a.u. the accuracy is limited by the difficulty of detecting these very low energy electrons. Thus, the discussion here will be generally confined to ejected electron velocities in the range ~ 0.5-3 a.u.
Figure 5.1: Ratios of experimental and theoretical cross sections for electron emission by 1, 3, and 5 MeV H\(^+\) impact on H\(_2\) for the electron observation angles indicated. The solid curves are obtained from Eq. (5.2) using analytical Born cross sections obtained from hydrogenic wave functions and the dashed curves are obtained from fits to the oscillatory function given by Eq. 5.1.
The spectra of Fig. 5.1 show distinct variations in the interference patterns with electron ejection angle. Moreover, the oscillatory structures vary with the collision velocity for all angles. At the forward angle of 30° the interference structure oscillates more slowly at 1 MeV than at 5 MeV. For 60°, the oscillatory structures display a similar collision velocity dependence as for 30°, with the oscillation frequency increasing with collision velocity. However, for this angle electron emission is largely influenced by binary encounters (see chapter 2), which explains the difficulty of observing oscillatory spectra at 60°. This effect is seen particularly at 1 MeV projectile energy where the wing of the binary encounter peak has a large impact over the entire electron energy range. On the other hand, for the backward angle of 150°, the opposite collision velocity dependence is seen with the interference pattern oscillating faster at the lowest projectile energy. Furthermore, the interference structure for 150° shows a significantly higher oscillation frequency than for 30° for all projectile energies. The 90° data show a similar collision velocity dependence as for 150° but with a much lower overall oscillation frequency.

The angular dependences are in qualitative agreement with predictions of the Born approximation as shown by solid curves in Fig. (5.1), although deviations in magnitude exist. Additionally, the collision velocity dependences agree with the trends of the Born predictions. These variations with electron emission angle and collision velocity can be traced to the dependences on $k_j = k \cos \theta_j$ and $q_{min} = \Delta E/\nu_r$ in the formulation of Nagy (Nagy et al., 2002), although the magnitudes of the observed oscillation frequencies are generally underestimated, particularly for 150°.

To obtain more detailed characteristics of the interference structures and the changing oscillation frequencies, the function
\[ f(k) = F \left[ 1 + \frac{\sin(kcd)}{kcd} \right] + G, \quad 5.2 \]

which represents Eq. (2.15), was used to fit the data of Fig 5.1. In this equation, \( F \) and \( G \) (with the constraint \( F+G=1 \)) are the interfering and non-interfering cross section fractions, respectively, and \( c \) is the frequency fitting parameter. This analytical function was fit to the normalized measured cross section ratios of Fig. 5.1 and the results are shown by the dashed curves. According to the formulation of Nagy et al. (Nagy, 2002), \( c \) is expected to be approximately equal to \( \cos \theta \) to the extent that \( q_{\text{min}} \) is small (although this approximation is not so accurate for 1-5 MeV H\(^+\)). From the figure, the measured cross section ratios are seen to be well represented by this function, and, consequently, the changes in the oscillation frequency with electron ejection angle can be quantitatively determined.

The values of the frequency parameter \( c \) obtained from the fits, along with the corresponding values of Stolterfoht et al. (Stolterfoht, 2003) for high velocity Kr\(^{33+}\) projectiles, are listed in Table 5.1 as plotted in Fig 5.2 as a function of the collision velocity (see Appendix). The analytical function given by Eq. 5.2 was also used to fit the Born approximation results (see Appendix). The table and the figure include these \( c \) values characterizing the Born approximation as well as the value of \( \cos \theta \) for comparison. The results show that the Born values follow the tendencies of the experimental values, although for 90\(^{\circ}\) and 150\(^{\circ}\) the fit values are underestimated. Examination of the frequency parameter \( c \) determined from the fit to the experimental results shows that the values of \( c \) (\( \approx \cos \theta \)) are generally larger than \( \cos \theta \), except for 60\(^{\circ}\), and in some cases exceed unity. This fact that \( c \) can be greater than unity seems to be particularly true for the backward angle of 150\(^{\circ}\), where it is found to have a value > 1.5. The reason for this apparently nonphysical result is not clear, but points
Table 5.1. Values of the frequency parameter $c$ as a function of the electron emission angle $\theta$ for 1, 3, 5 MeV $H^+$ and 68 MeV/u $Kr^{33+}$ (Stolterfoht et al., 2003) projectiles impacting on $H_2$. The values of $\cos \theta$ are shown for comparison. Values of $c$ obtained from Stolterfoht et al. are marked with the symbol §.

<table>
<thead>
<tr>
<th>Electron emission angle, $\theta$</th>
<th>$\cos \theta$</th>
<th>$H^+$ on $H_2$</th>
<th>$Kr^{33+}$ on $H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 MeV</td>
<td>3 MeV</td>
</tr>
<tr>
<td>$30^\circ$</td>
<td>0.87</td>
<td>0.75</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td>0.72</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$60^\circ$</td>
<td>0.50</td>
<td>0.23</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td>0.24</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$90^\circ$</td>
<td>0</td>
<td>0.44</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td>0.33</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$150^\circ$</td>
<td>0.87</td>
<td>1.82</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td>1.27</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>theory</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
to inadequacies in the existing theoretical formulations of the observed interference phenomena. On the other hand, for the observation angles of 30° and 60°, the $c$ values are reproduced quite well by those obtained from the Born approximation although deviations from $\cos \theta$ exist depending on the collision velocity. For 90°, the nonzero values of $c$ support the observation that the oscillatory structure does not diminish completely. Thus, at this angle binary encounter processes do not account for all of the electron emission (see discussion below).

![Figure 5.2: Experimental and theoretical values of the frequency parameter $c$ (from Table 5.1) displayed as a function of collision velocity, $v_p$ in atomic units. The solid symbols represent the experimental $c$ values obtained from fits to Eq. 5.2 and the empty symbols are the theoretical results from the theoretical Born approximation (see text).](image-url)
To gain more information about the oscillation frequency and its dependence on the projectile energy, the \( c \) values obtained from experimental results have been plotted logarithmically as a function of projectile velocity, \( v_p \) as shown in Fig. 5.3. For electron emission angles 30° and 60°, the frequency parameter \( c \) is found have a velocity dependence nearly proportional to \( \ln(v_p)^{1/4} \) except at the lowest velocity. On the other hand, for 90° and 150°, the \( c \) values show an inverse dependence of \( \ln(v_p)^{1/4} \), although for 90° the agreement with this dependence is very approximate.

Figure 5.3: Frequency parameter \( c \) extracted from the experimental fit values (see Table 5.1) displayed logarithmically as a function of collision velocity, \( v_p \) in atomic units. The solid symbols represent the experimental \( c \) values and the dashed lines represent the function \( \text{const.} \times \ln(v_p)^{1/4} \) and the dotted lines the function \( \text{const.} \times 1/\ln(v_p)^{1/4} \).
Calculated Results

To better compare the experimental results with the predicted theoretical trends, calculations have been carried out for 1, 3, and 5 MeV H⁺ on the H₂ collision system in the framework of the Born approximation. Since the overall cross sections for electron emission from H₂ decrease rapidly with ejected electron energy (see chapter 4) while the interference term varies by only a factor of 2, it is convenient to normalize the oscillatory cross sections for H₂ to the corresponding cross sections for two independent H atoms integrated over \( \bar{q} \), i.e.,

\[
\left( \frac{d^2 \sigma_{H_2}}{d\Omega de} \right)_{\text{norm}} = \frac{d^2 \sigma_{H_2}}{d\Omega de} / \int d^3 \sigma_{2H} \frac{[1 + \sin [\bar{k} - \bar{q}]d]}{|\bar{k} - \bar{q}|d} d\bar{q} / \int d^3 \sigma_{2H} d\bar{q} 5.3
\]

where \( d\Omega \) and \( de \) are the solid angle and energy of the outgoing electron. The cross section \( \sigma_{H_2} \) denotes the two-center electron emission and \( \sigma_{2H} \) independent emission from the two H atoms. The sinusoidal term represents the interference due to coherent emission from the two centers, where \( \bar{k} \) is the outgoing electron velocity, \( \bar{q} \) the momentum transfer, and \( d \) the molecular internuclear distance.

Numerical calculations were performed using Eqs. 2.12 - 2.15 in conjunction with analytical Born approximation cross sections for atomic H (Eq. 2.5), using hydrogenic wave functions with an effective target charge of \( Z_t = 1.19 \), which comes from a variational principle treatment (Galassi et al., 2002). Normalized cross section ratios obtained from Eq.(5.3), giving the interference structures are plotted as a function of electron velocity \( k \) (in atomic units, the electron momentum and velocity are equal) in Fig. 5.4 for 3 MeV H⁺ on H₂ for 30°, 45°, 60°, 90° and 150° observation angles. These theoretical results show that the oscillatory pattern has a period that changes significantly with the electron observation angle. In particular, these
Figure 5.4: Calculated double differential cross section (DDCS) ratios from Eq. 5.3 showing the expected interference structure resulting from the ionization of H$_2$ by 3 MeV H$^+$ impact as a function of electron velocity for the emission angles 30°, 45°, 60°, 90° and 150°.
calculations show a strongly decreasing oscillation frequency with increasing observation angle up to 90°. On the other hand, the frequency for 150° is higher than for the symmetric forward angle of 30°. Thus, first-order interference effects are expected to be most obvious at forward and backward angles that do not deviate too much from the beam direction.

The theoretical results also exhibit a variation in the oscillatory structure with the projectile energy for forward and backward angles as shown in Fig. 5.5. At the forward angle of 30° the predicted interference structure oscillates more slowly at 1 MeV than at 5 MeV. On the other hand, for the backward angle of 150°, the opposite dependence is seen with the interference pattern oscillating slightly faster at the lower projectile energy. Furthermore, the interference structure for 150° shows a significantly higher oscillation frequency than 30° for both projectile energies. The 90° results show a similar collision energy dependence as for 150° but with a much lower overall oscillation frequency, especially for 5 MeV. At 90° electron emission is strongly dominated by binary encounters (Stolterfoht et al., 1998) (see Fig. 2.2) with the result that interference structures are expected to diminish.

A question arises concerning use of the effective target charge \( Z_t = 1.19 \) for the denominator of Eq. (5.3). Since \( \text{H}_2 \) and \( \text{H} \) have different velocity distributions for the bound electrons, i.e., Compton profile, the differential cross section ratio excluding the oscillatory part \( [1 + \sin(pd)/pd] \) of the \( \text{H}_2 \) cross section (i.e., with this term set to unity) might contribute additional structure. Calculated ratios are shown in Fig. 5.6 for 1 MeV \( \text{H}^+ \) impact on \( \text{H}_2 \) and \( \text{H} \) at 30°, 45° and 60° ejection angles for electron velocities up to about 12 a.u., using effective charges of \( Z_t = 1.19 \) and \( Z_t = 1 \) for the molecular and atomic targets, respectively.
The calculated ratios take into account the differences in the Compton profiles for H₂ and H (see Fig. 5.3) but without any effect due to interference. For the angles shown in Fig. 5.6, the ratio shows a dip due to the larger maximum value of the Compton profile for H compared to H₂ at the position of the binary encounter peak. On the other hand, the broad maxima below these dips are due to the larger values of the shoulders of the Compton profile for H₂ compared to H. Therefore, these features which are due solely to the differences in the Compton profiles of H₂ and H, have a completely different origin than the oscillatory interference structures (Galassi et al., 2002). However, the predicted theoretical interference results (including the
oscillatory term) display oscillatory structures (see Figs. 5.4 and 5.5) exclusively from
the interference of the ejected electrons that are bound to identical atomic centers of
\( \text{H}_2 \) because effects due to Compton profile differences are cancelled in the ratio if the
same effective charge \((Z_e = 1.19)\) is used in the numerator and denominator of Eq. 5.3.

![Graph](image)

**Figure 5.6:** Ratios of the normalized differential cross section from Eq. 5.3 excluding
the oscillatory term \([1+\sin(pd)/pd]\) (i.e., set to unity) evaluated with the effective
charges \(Z_e = 1.19\) and \(Z_i = 1\) for molecular and atomic targets, respectively. The
calculated ratios are obtained for 1 MeV \(\text{H}^+\) impact on \(\text{H}_2\) and \(\text{H}\) at 30°, 45° and 60°
ejection angles. The arrows show the central position of the binary encounter peaks
for the electron ejection angles indicated.
To determine the relative contributions to the measured cross sections from dipole and binary transitions as discussed in chapter 2, an analytic expression for electron emission by proton impact in the first Born approximation (Landau and Lifschitz, 1958) has been evaluated. This cross section is differential in the momentum transfer $q$, the ejected electron momentum $k$, and the solid angle $\Omega$. The calculated cross sections can be separated into dipole and binary parts by using the intermediate momentum transfer $q_0$ as suggested by Bethe (see chapter 2). Calculated relative contributions from dipole and binary transitions for 5 MeV $H^+$ impact are shown in Fig. 5.7 as a function of electron velocity for the electron emission angles $30^\circ$, $60^\circ$, $90^\circ$ and $150^\circ$. The figure shows that the contributions of the dipole and binary parts change considerably with the ejected electron angle and electron velocity. These results indicate the dominance of dipole transitions over the entire electron velocity range at the emission angle of $30^\circ$. For $150^\circ$ observation angle, dipole transitions dominate for electron velocities less than $\sim 3.0$ a.u., after which binary contributions dominate. For $90^\circ$, binary processes account for nearly all of the electron emission over the entire electron velocity range, a result which explains the difficulty of observing oscillatory structure at the electron emission angle of $90^\circ$ and other intermediate angles such as $60^\circ$. Furthermore, for the present collision system the dominance of dipole transitions for symmetric angles with respect to $90^\circ$ are expected to be nearly equal up to $\sim 2.5$ a.u.. Thus, interference effects are expected to be most apparent at forward ($30^\circ$) and backward angles ($150^\circ$) with weaker oscillatory features at intermediate angles, in agreement with the experimental results shown above.

Even though the present experimental data and the Born approximation results for the primary interference structures are in quite reasonable agreement, there are
Figure 5.7: Relative contributions of dipole and binary transitions for the observation angles of 30°, 60°, 90° and 150° for electron emission from H₂ by 5 MeV H⁺ impact calculated from the triply differential cross sections (Landau and Lifschitz, 1958).
noticeable discrepancies for electron velocities lower than ~1 a.u. where the Born approximation fails to reproduce the trend of the experimental data. These deviations may be caused by the approximate one-center wave functions used for the final state. According to Stolterfoht et al. (Stolterfoht, 1997) and Fainstein et al. (Fainstein, 1991) for ionization in ion-atom collisions, the outgoing electron is ejected into a final continuum state of a two-center potential due to the Coulomb fields of the projectile and ionized atom. Therefore, correct two-center wave functions are needed for the ejected continuum electron for a more accurate comparison of the theory with the experimental results.

Second-order Interference

Closer examination of the measured cross section ratios reveals the existence of reproducible higher frequency structures and oscillations superimposed on the main oscillatory structure. To see these more clearly, the normalized cross section ratios from Fig. 5.1 have been divided by their corresponding fits to give the results shown in Figs. 5.8, 5.9, 5.10 and 5.11 for 30°, 60°, 90°, 150°, respectively, for each of the beam energies measured. These latter data were then fit to a function of a form similar to that of Eq. 5.2, specifically,

\[ g(k) = A[1 + \sin(kc'd + \phi')/(kc'd + \phi')] + B \]  \hspace{1cm} 5.4

with \( A+B=1 \) and allowance for a phase shift \( \phi' \), to determine the frequency parameter \( c' \) for the secondary oscillations. The resulting fits are shown as the solid curves in the Figs. 5.8-5.11 and the values of \( c' \) and \( \phi' \) obtained from the fitting for 1, 3, 5 MeV H\(^+\) projectiles are summarized in Table 5.2. The \( c' \) values are about a factor of three larger than those found for the primary oscillatory structure and vary slightly

65
Table 5.2. Values of the frequency parameter $c'$ and phase shift $\phi'$ as a function of the electron ejection angle $\theta$ for 1, 3, 5 MeV H$^+$ projectiles impacting on H$_2$.

<table>
<thead>
<tr>
<th>Collision Energy</th>
<th>$\theta$</th>
<th>$c'$</th>
<th>$\phi'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 3, and 5 MeV H$^+$</td>
<td>$30^\circ$</td>
<td>2.9</td>
<td>$\pi$</td>
</tr>
<tr>
<td></td>
<td>$60^\circ$</td>
<td>2.9</td>
<td>$\pi$</td>
</tr>
<tr>
<td></td>
<td>$90^\circ$</td>
<td>3.3</td>
<td>$\pi$</td>
</tr>
<tr>
<td></td>
<td>$150^\circ$</td>
<td>2.7</td>
<td>$\pi$</td>
</tr>
</tbody>
</table>

with electron observation angle, while the phase shifts $\phi'$ are constant with the value $\pi$. Moreover, it is evident from Figs. 5.8-5.11 (see Appendix) that the frequency parameter $c'$ of the secondary oscillations does not vary with the collision velocity.

From Eq. 2.24, it is recalled that the secondary oscillatory structure is expected to have a frequency about double that of the primary structure at forward angles where dipole transitions with $q \approx 0$ dominate. For binary encounter collisions with $q \approx k$, the second order should also show an approximate doubling of the oscillation frequency. However, the second-order effects are seen to occur with oscillation frequencies that are nearly triple that of the primary structure for $c \sim 1$ (i.e., near $30^\circ$). Second-order structures are also expected to be most pronounced at $90^\circ$ (and to a lesser extent at $60^\circ$) where electron emission by binary encounter processes dominates.

The origin of the secondary oscillations has been interpreted from phase differences using methods known from wave optics (see chapter 2). From such an analysis, the secondary oscillations are attributed to interference of the primary ejected electron wave with the secondary wave that results from scattering at the other atomic center, an effect that has no analogy in Young’s two-slit experiment. Despite the fact that the qualitative features of this secondary scattering can be
derived from the wave optics formalism, the approximations required to carry out the theory limit a quantitative comparison with experiment (Stolterfoht et al., 2004, Stolterfoht and Sulik, 2004). Hence, the characterization of these secondary oscillations remains a significant challenge.

**High-frequency Oscillation**

The ratios shown in Figs. 5.8-5.11 also suggest the existence of still higher frequency structures superimposed on the second-order oscillatory structure. In order to examine these structures more clearly, the “measured” cross section ratios from Figs. 5.8-5.11 have been divided by their corresponding fits to give the results shown in Figs. 5.12, 5.13, 5.14, and 5.15 for electron emission at 30°, 60°, 90° and 150°, respectively, for 1, 3, and 5 MeV projectiles. Figure 5.16 shows these same ratios at 30°, 60°, 90°, and 150° for 3 MeV H⁺ ions. From these figures, high-frequency oscillations do not appear to exhibit a significant dependence on either the collision velocity or the electron emission angle.

To quantify these high-frequency oscillatory structures the measured ratios of Figs. 5.12 – 5.15 were fit to a function of the form similar to that of Eq. 5.4, specifically,

\[
h(k) = 1 + \left[ A' \frac{\sin(kc'd + \phi')}{kc'd + \phi'} + B' \sin(kc''d - \phi'') \right], \tag{5.5}
\]

where the first term in brackets represents the slower second-order oscillations of frequency \(c'\) and the second term the much higher frequency oscillations with frequency parameter \(c''\) and phase shift \(\phi''\).
Figure 5.8: Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 30° electron observation angle for 1, 3, and 5 MeV H⁺ impact. The fit to the data with Eq. 5.4 yields a value for the frequency parameter of $c' = 2.9$. 

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Figure 5.9: Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at $60^\circ$ electron observation angle for 1, 3, and 5 MeV H$^+$ impact. The fit to the data with Eq. 5.4 yields a value for the frequency parameter of $\omega' = 2.9$. 

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Figure 5.10: Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 90° electron observation angle for 1, 3, and 5 MeV H⁺ impact. The fit to the data with Eq. 5.4 yields a value for the frequency parameter of \( c' = 3.3 \).
Figure 5.11: Cross section ratios from Fig. 5.1 divided by the fit function of Eq. (5.2) showing the second-order oscillatory structure as a function of electron velocity at 150° electron observation angle for 1, 3, and 5 MeV H⁺ impact. The fit to the data with Eq. 5.4 yields a value for the frequency parameter of $c' = 2.7$.

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To fit the data of Figs. 5.12 – 5.15, the full expression given by Eq. 5.5 was used. In the fitting the frequency parameter \( c' \) and the phase shift \( \phi' \) were held constant at the values found for the fits to the second-order interference data (Table 5.2), while the constants \( A' \) and \( B' \) were varied to match the amplitude of the data. From the fitting it is found that \( c'' \approx 20 \) with a phase shift \( \phi'' \approx \pi/2 \) for each of the electron emission angles and for each collision energy. Moreover, the high frequency structure oscillations are essentially independent of the collision velocity and the electron ejection angle.

From the fits the high-frequency oscillation intervals are found to occur for \( \Delta k \approx 0.25 \) a.u.. The question then arises as to the origin of these high-frequency oscillations. Several possibilities are considered:

(a) *Quantum beats* (Macek, 1969, 1970), result when electron emission occurs from collisionally excited adjacent fine-structure levels. Since the high-frequency structure is found to not depend on the collision velocity, quantum beats are not likely to be the cause of these oscillations.

(b) *Vibrational excitation* of \( \text{H}_2^+ \) during the ionization process, as observed for incident electrons (von Busch and Dunn, 1972) and by intense laser fields (Urbain et al., 2004), gives rise to equally spaced energy levels, which might result in an oscillatory structure. However, the separation of these vibrational levels is just a fraction of an electron volt (~ 0.5 eV). Such a separation is too small to account for the observed repetition interval of the high frequency oscillations in the present work, which, additionally appear to occur for a constant interval \( \Delta k \). Furthermore, the collision time (~0.1 a.u.) is too short to appreciably excite these vibrational excitations, thereby ruling out the possibility of rotational excitations for the same reason.
Figure 5.12: Cross section ratios of Fig. 5.8 divided by the corresponding fit curves, showing the existence of high-frequency oscillations superimposed on the second-order structure. The solid curves are the fitted high-frequency oscillations from Eq. (5.5), and the dashed curves are the second-order fits from Eq. (5.4). The fit to the data with Eq. 5.5 yields a value for the frequency parameter of $c''$ about 20.
Figure 5.13: Cross section ratios of Fig. 5.9 divided by the corresponding fit curves, showing the existence of high-frequency oscillations superimposed on the second-order structure. The solid curves are the fitted high-frequency oscillations from Eq. (5.5), and the dashed curves are the second-order fits from Eq. (5.4). The fit to the data with Eq. 5.5 yields a value for the frequency parameter of $c''$ about 20.
Figure 5.14: Cross section ratios of Fig. 5.10 divided by the corresponding fit curves, showing the existence of high-frequency oscillations superimposed on the second-order structure. The solid curves are the fitted high-frequency oscillations from Eq. (5.5), and the dashed curves are the second-order fits from Eq. (5.4). The fit to the data with Eq. 5.5 yields a value for the frequency parameter of \( c'' \) about 20.
Figure 5.15: Cross section ratios of Fig. 5.11 divided by the corresponding fit curves, showing the existence of high-frequency oscillations superimposed on the second-order structure. The solid curves are the fitted high-frequency oscillations from Eq. (5.5), and the dashed curves are the second-order fits from Eq. (5.4). The fit to the data with Eq. 5.5 yields a value for the frequency parameter of $c^*$ about 20.
Figure 5.16: Cross section ratios from Figs. 5.8, 5.9, 5.10, and 5.11 divided by the corresponding fits for 3 MeV H\(^+\) projectiles. The solid curves are the fitted high-frequency oscillations from Eq. (5.5), and the dashed curves are the second-order fits from Eq. (5.4). The fit to the data with Eq. 5.5 yields a value for the frequency parameter of $\omega''$ about 20.
(c) Stückenberg oscillations (Dai et al., 2003, Saha, 1993, and references therein), which have their origin in interferences resulting from different quasimolecular states that lead to the same final (ionization) state, are not likely to be the source of the high-frequency oscillations because these oscillations are expected to occur for much lower collision velocities.

(d) Also, the possibility of electron correlation might be considered owing to the fact that there are initially two electrons on the H₂ molecule (Walter and Briggs, 1999). It is well known that electron correlation can play a significant role in the excitation or ionization of a second electron following an initial interaction between the incident ion and the primary ejected electron (McGuire, 1997). However, while the specific effect of correlation on the observed interference structure is not known, it seems unlikely that it could give rise to the high frequency oscillations observed here.

Although a definitive answer as to the origin of the high-frequency oscillations cannot be given, the following possibility is considered: We note that H⁺ + H₂ collisions are unique in that there are three atomic centers involved in the ionization process, consequently, the incoming H⁺ ion might act transiently as one of the identical atomic “centers” from which the electron is coherently ejected. Furthermore, most of the ionization events take place at large impact parameters (Inokuti, 1971) (i.e., much greater than the internuclear distance d) for the collision velocities used here. Then, if the incoming H⁺ ion acts in combination with one of the existing H₂ centers as an additional “molecule” from which electron ejection occurs, this effective molecule has a much larger internuclear spacing, which in turn gives rise to a much smaller value of the electron momentum k for one complete oscillation of the interference structure (since kd ~ 2π). This picture of the origin of the high-
frequency oscillation has a direct analogy with two-center (projectile-target) electron emission, where the outgoing electron is emitted into a final continuum state of the two-center potential due to the Coulomb fields of the projectile and the ionized atom. In such a scenario, the high frequency oscillation is due to the interference between electron amplitudes associated with direct ionization and ionization followed by postcollisional deflection. For a high-frequency oscillation interval $\Delta k \sim 0.25$ a.u., as noted above, the predicted internuclear spacing of the transient $H^+ + H$ molecule is about 25 a.u., a value that is consistent with the expectation of large impact parameter collisions.

Furthermore, at large impact parameters electron emission occurs mainly from the transient molecule oriented with its internuclear axis perpendicular to the beam direction simply because ionization is most probable when the ion passes at its distance of closest approach. Such an orientational effect would be expected to reduce the damping of the oscillations that occur for randomly oriented molecules (as in Eq. 2.12). From Figs. 5.12 – 5.16, the high frequency oscillations do not appear to be strongly damped, in contrast to the primary oscillatory structures shown in Figs. 5.1, and thereby giving additional support to this transient molecule explanation.

In order to verify the origin and the existence of these high-frequency oscillations, it would be important to show that this oscillation is absent for projectiles other than $H^+$ interacting with $H_2$. However, if similar oscillations occur for other projectiles, then these high-frequency oscillations should also be observable in electron emission from the transient molecules formed in collisions of fast ions with atomic targets. These latter cases need to be explored experimentally, and theoretically as well.
Future Prospects

New measurements are needed to provide insight into the reasons for the existing discrepancies between experiment and theory for the first-order oscillations, and to better characterize the nature of the second-order and high-frequency oscillations. Several possibilities for future work are considered.

(a) \( H^+ + N_2 \) - An extension of the present work for \( H^+ + H_2 \) collisions to \( N_2 \) targets is similar to that of \( H_2 \). In this system, the electron ejection will occur primarily from the valence shell with a binding energy close to that of \( H_2 \). However, the internuclear separation of \( N_2 \) is larger than that of \( H_2 \) (2.1 a.u. compared to 1.4 a.u.). Due to large internuclear separation of \( N_2 \), a full oscillation of the interference structure is expected for electron energies ranging from about 0-125 eV (instead of 0-250 for \( H_2 \)).

(b) \( H^+ + HD \) – Another good choice for experiment is to determine if interference effects exist for HD molecules. Although each center of HD carries the same charge and the binding energy is nearly the same as for \( H_2 \), the atomic centers are not identical. So, study of electron emission from this molecule would help to determine whether the non-indistinguishibility of the HD atomic centers destroys the coherence of the emitted electrons. Therefore, it is important to investigate this collision system and at the same time determine if interference effects survive.

(c) \( H^+ + C_2H_2 \) - An interesting case for future investigation of interference effects relates to the existence of more than two scattering centers. A particularly good candidate for study is the linear acetylene molecule \( C_2H_2 \) (DuBois, 2003). For \( C_2H_2 \) the H–C separation is 2.0 a.u. and the C–C separation is 2.3 a.u.. Because of two different pairs of identical atomic centers, interference effects might
be enhanced. Furthermore, the different pairs of identical centers might produce second-order oscillations as have been observed for H$_2$.

(d) $e^- + H_2$ - Messiah showed in his formulation that interferences should exist for electrons scattered from H$_2$ (Messiah, 1970). It is an excellent choice to study interference from electrons scattered from H$_2$ rather than *ejected*, i.e., ionized, electrons. This textbook example of electron interferences has never been investigated.

Additional work is needed to verify both the existence and the origin of the observed high-frequency oscillations. Two studies that could provide new insight are the following:

(e) C$^6^+$ + H$_2$ - As a follow up of this new finding, it is important to know whether the origin of the high-frequency oscillations is due to the formation of a transient "molecule" consisting of identical atomic centers formed by the projectile and one of the atomic centers of the target molecule. Thus, an obvious choice for a new measurement would be a different incident particle, e.g., C$^6^+$. If there are no high frequency oscillations for C$^6^+$, then the origin of these interferences would point towards formation of this transient molecule. On the other hand, if the high-frequency oscillations persist in this collision system, the incident particle doesn’t have to be identical and the oscillations might be due to the two-center projectile-target effect when the fields of both collision partners are significant for the ejected electron.

(f) He$^{2+}$ + He - Another interesting case to investigate is electron emission from an atomic target (e.g., He) caused by incident He$^{2+}$, for which interferences were not previously observed experimentally (Duncan *et al.*, 1977). In this collision process, high-frequency oscillations could arise from the coherent sum of different
electron emission mechanisms, such as direct ionization of the target and capture to
the continuum of the projectile. However, if this type of collision system does not
show any signature of high-frequency oscillations, the origin of these interferences
would point towards formation of a transient molecule consisting of identical
particles.
CONCLUSIONS

The present measurements, conducted at Western Michigan University using the tandem Van de Graaff accelerator, focus on the ionization of H\textsubscript{2} by 1, 3 and 5 MeV H\textsuperscript{+} impact. Primary (first-order) and secondary (second-order) interference effects have been studied in the spectra of electrons ejected coherently from the identical atomic centers of H\textsubscript{2}. The former phenomenon is analogous to Young-type interferences with the slits replaced by the atomic centers, but the latter case, which has been attributed to interference of the primary wave corresponding to electron ejection with this same wave after backscattering at the other atomic center, has no analogy in Young’s experiment. The observation of much higher frequency oscillations, superimposed on the first- and second-order interference structures, and reported here for the first time, are suggested to be due to the interference between electron amplitudes associated with direct ionization and ionization followed by postcollisional scattering.

The oscillatory interference features are revealed as a function of the ejected electron velocity for observation angles 30°, 60°, 90° and 150° with respect to the incident beam direction. It was shown that dipole transitions, which are dominant at high velocities and relatively small ejection angles, are responsible for the first-order interference effects. On the other hand, binary encounter electrons dominate near 90° emission angle, and, consequently, interference structures diminish. The observed first-order interference structures exhibit variations in the oscillation frequency with the electron observation angle and projectile velocity in general agreement with Born predictions, although significant deviation exist.
Division of the primary oscillatory structures by the corresponding fit curves reveals second-order oscillations with an enhanced frequency. Fits to these secondary oscillations give frequencies that are about a factor of three larger than those for the primary structures and show a slight variation with the electron observation angle, but no variation with the projectile velocity. Finally, the cross section ratios show striking evidence for still higher-frequency oscillations (about a factor of 20 higher than the primary structures) superimposed on the second-order structures. A tentative explanation for the high-frequency oscillations is given in terms of coherent emission from the transient molecule formed in combination with the passing H\(^+\) projectile.

These various results point to a range of unique phenomena, still largely not understood, associated with electron emission from identical atomic centers. Future studies should focus on a better understanding of the origin of the frequency difference between the first- and second-order oscillations, along with future investigations of the newly observed higher frequency oscillations superimposed on the second-order interference structure.
APPENDIX

Error Analysis

The maximum likelihood method is the most general method for parameter estimation of statistical data (Cramer, 1958). The strength of this method is particularly displayed when there is only one set of data available, a situation that is very common in natural phenomena. The method of least squares which can be derived from the maximum likelihood theorem is suitable for repeatable data sets. These two methods are briefly reviewed below (Hagiwara, 2002, Bevington and Robinson, 1992).

The method of maximum likelihood: The likelihood \( L \) is defined as the joint probability density of a test p.d.f. \( f(x, \alpha_n) \), for which we want to estimate the parameter set \( \alpha_n \), evaluated at all independently measured data points \( x \).

\[
L(\alpha_n) = \prod_i f(x_i, \alpha_n).
\]  
\[\text{A.1}\]

The logarithm of the above equation gives the sum of the logarithms of the test at all \( x \).

\[
\ln L(\alpha_n) = \sum_i \ln f(x_i, \alpha_n).
\]  
\[\text{A.2}\]

To find the parameters \( \alpha_n \), one needs to maximize the log-likelihood value with respect to the unknown parameters:

\[
\frac{\partial \ln L}{\partial \alpha_n} = 0.
\]  
\[\text{A.3}\]

The parameters found by solving the above equation, called the likelihood equation, give the best fit model to data.
The method of least squares: This method is particularly useful for analyzing experimental data, where repeated measurements are possible at each data point. Suppose there are \( N \) measurements at each data point \( x_i \). Typically, the measured values \( y_i \) at the \( i \)-th data point (for \( j \) measurements) are Gaussian distributed with mean \( \langle y_i \rangle = \sum_j y_{i,j} / N \) and variance \( \sigma_i^2 = \sum_j (y_{i,j} - \langle y_i \rangle)^2 / (N - 1) \). The definition of \( \chi^2 \) is then

\[
\chi^2 = \sum_i \frac{[y_i - f(x_i, \alpha)]^2}{\sigma_i^2}.
\]

This value of \( \chi^2 \) must then be minimized for each of the parameters \( \alpha_n \) similar to the likelihood equation.

\[
\frac{\partial \chi^2}{\partial \alpha_n} = 0.
\]

The \( \chi^2 \) value calculated with the minimized parameters \( \alpha_n \) gives an estimate of the goodness of fit. If this value divided by the number of degrees of freedom is less than 1 then the test p.d.f. is considered to be a good fit to the data.

Application to experimental data: First-order interference structures were compared with an analytical fit function in order to extract frequency parameters to obtain specific information about the oscillation frequencies. In all cases, a weighted Bessel fit has been used. Hence, the method of least squares is used to recheck the accuracy of the estimated frequency parameters. Discussion of the statistical findings will be limited to 1 MeV \( \text{H}^+ \) on \( \text{H}_2 \) at 30° observation angle, for which there were 29 measurements at each data point thereby generating 29 separate data sets. Each data set was normalized by dividing with a theoretical cross-section formula for \( \text{H}^+ \) on \( \text{H} \) (times 2) (Eq. 2.5). This procedure reveals the interference effect due to the \( \text{H}_2 \) molecule compared to 2 hydrogen atoms.
The mean \( \langle y_i \rangle \) and variance \( \sigma_i^2 \) have been calculated from the \( N = 29 \) measurements at each data point \( i = 1, \ldots , 151 \). While it is generally not good practice to leave out experimental data points, large systematic errors may warrant excluding some data points. Thus, the following cross-section formula for first-order interference was fit using the method of least squares in the range \( i = 25, \ldots , 151 \) (below the 25\( \text{th} \) data point the accuracy was limited by the exponential difficulty to detect low energy electrons).

\[
F_1(x, D, c) = \left( 1 + D \frac{\sin(xcd)}{xcd} \right)
\]

Here \( c \) is the frequency parameter, \( d = 1.42 \) a.u. is the fixed intermolecular distance of \( \text{H}_2 \) and \( D \) is a normalization factor. After minimizing the \( \chi^2 \) value with respect to the parameters, the values \( c = 0.77 \) and \( D = 0.47 \) were obtained, which is almost the same value for the frequency parameter \( c \) as that listed in Table 5.1 for 1 MeV \( \text{H}^+ \) at 30° observation angle. The corresponding fit (solid curve) is plotted in Fig. A.1 along with the data points \( \langle y_i \rangle \) and the error bars \( \sigma_i^2 \).

The data points of Fig. A.1 were then divided by the fit to the first order interference formula (Eq. A.6) to determine if there is any additional structure in the data and the results are shown in Fig. A.2. Once a model is chosen to fit these new data, the errors calculated from the original data cannot be used since the repeatability of the data set, divided by the fitted model, is lost. However, one can use the maximum likelihood method to fit any model.

Then, the model for the additional structure can be written as

\[
F_2(x, A, B, c', \phi') = A \left( 1 + \frac{\sin(xc'd + \phi')}{xc'd + \phi'} \right) + B
\]

where \( \phi' \) is a phase factor typically on the order of \( \pi \), and the normalization factors \( A \) and \( B \) are arbitrary and satisfy the relationship \( A + B = 1 \).
Equation A.7 was then fit to the data of Fig. A.2 (data of Fig. A.1 divided by its fit). The fit (solid curve) is plotted with adjustable parameter $c' = 2.88$ keeping the normalization parameters $A = 0.4$ and $B = 0.6$ fixed.
Figure A.2: Cross section ratios compared with the fit (solid curve) obtained by the maximum likelihood method to obtain the frequency parameter $c'$. The graph shows experimental data for 1 MeV $H^+$ impact on $H_2$ at $30^\circ$ electron observation angle.
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