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Received 12 November 1970

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Comparison of Experimental and Theoretical Values of Cross Sections for Electron Production by Proton Impact*

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Angle and energy distributions of electrons ejected from single- and multishell atoms by 50-to 300-keV protons are compared with various theoretical treatments. Partial cross sections for each subshell are calculated by scaling according to the number of electrons and the binding energy and then are added. The Born approximation fails at large and at small angles but yields fair agreement at intermediate angles. The treatments of Salin and of Macek, which take account of the influence of the projectile after the collision, yield much improved agreement at small angles. The binary-encounter model is used to calculate cross sections which are differential only in electron energy. An analytical expression is given for the binary-encounter cross section averaged over the Fock hydrogenic distribution of orbital velocities. When the average orbital energy is calculated from Slater's rules, the results agree somewhat better with experiment than when this energy is set equal to the binding energy.

I. INTRODUCTION

The major theoretical methods used to describe the process of ionization by proton impact have been the first Born approximation and the binary-encounter approximation. These yield reasonably good values of total cross sections if the velocity of the proton is somewhat greater than the average velocity of the orbital electrons in the target. The agreement is not good, however, at lower proton velocities, nor are the finer features of the process, such as the angular distribution of the ejected electrons, accurately described by existing theories. Considerable theoretical progress in both quantum and binary-encounter theories has been made by comparison with doubly differential cross section (ddcs) measurements in which the distribution over angle and energy of ejected electrons is determined. We have previously had experimental data only on atomic systems with just one shell. Data of Crooks and Rudd¹ with four different multishell targets allow us to assess the applicability of the various theoretical methods to more complex systems.

In this paper, we review the progress made in using the Born approximation and present results for multishell targets using Born calculations with hydrogen ground-state wave functions, scaling according to the binding energy and number of electrons for each shell, and adding the partial cross sections. Section II contains similar calculations using instead the theories of Salin² and Macek³ which take into account the recently proposed mechanism of charge transfer into continuum states. Finally, the application of the binary-encounter model to this type of collision is discussed, and an equation is given for cross sections integrated over the Fock hydrogenic distribution of orbital velocities. This

equation is applied to multishell systems and compared with experiment.

From these comparisons, a fuller understanding of the role of various mechanisms of electron production is emerging.

II. BORN APPROXIMATION

Kuyatt and Jorgensen⁴ made the first ddcs measurements and also presented an equation for calculating them based on the first Born approximation and hydrogenic wave functions. By scaling this equation, calculations were made by Rudd, Sautter, and Bailey⁵ and were compared to their helium and hydrogen measurements. Even at the highest energy, 300 keV, the agreement was not good. The energy distribution of electrons integrated over all angles of ejection was fairly well predicted this way, but errors in the ddcs of factors of 10 were still present.

Since ddcs data for proton impact on hydrogen atoms were not yet available, the question arose of whether the failure was due to the scaling, the inadequacy of the Born approximation, or something else. This question was partially answered in the work of Oldham⁶ in which he used improved helium wave functions instead of scaling from hydrogen. Some improvement was noted, especially when the final-state wave function was taken to be a hydrogenlike continuum modified by replacing the l=1 part with a Hartree-Fock continuum. However, substantial discrepancies still existed in the forward and backward directions, leading to the conclusion that the entire error could not be ascribed to inaccurate wave functions.

We inquire here what effect the presence of inner shells has on the agreement of the Born results and experiment. The Kuyatt equation⁴ has been used by calculating the partial cross sections for each subshell, scaling in each case by the binding energy, multiplying by the number of electrons in each subshell, and adding these partial cross sections. The resulting energy distribution integrated over all angles agrees well with experiment as shown in Fig. 1 for 200-keV protons on nitrogen, but as with single-shell targets the results are much less satisfactory when we compare distributions over angle as in Fig. 2 for argon. In agreement with experiment, the cross section generally falls off with increasing electron energy and increasing angle, and the momentum-energy conservation maximum is at about the right energy although it is considerably overpredicted in height. However, the calculated cross sections are much too low at small and at large angles. To investigate the angular distribution further, we have plotted the calculated partial cross sections for each shell in Fig. 3 for 500eV electrons ejected from nitrogen. The 1s shell is expected to contribute little to the cross section at small angles but becomes dominant at angles above 70°. This is in agreement with the empirical observation of Paper I that electrons from shells with large binding energies are ejected more strongly in the backward direction. However, the calculations at large angles are too low by an order of magnitude, and at lower electron energies the contribution expected from the 1s shell is relatively still smaller.

Not only are the experimental cross sections in the backward hemisphere much larger than predicted, in some cases (see, e.g., Fig. 2 of Paper I) they even increase slightly with increasing angle. This effect is at variance with all the simple the-

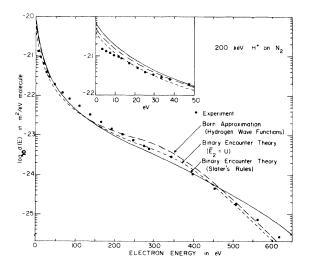


FIG. 1. Cross sections for electron production integrated over all angles. Experimental values compared with Born approximation and with binary-encounter calculations integrated over the Fock distribution of orbital velocities.

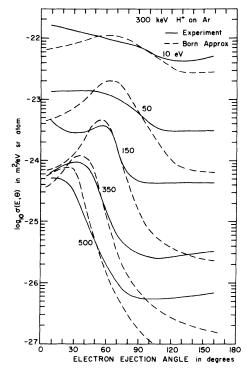


FIG. 2. Angular distribution of electrons of various energies from 300-keV protons on argon. Comparison of experiment and Born calculations.

ories.

Many of the angular distributions show an abrupt change of slope at 90°, suggesting that there is an additional mechanism of electron ejection which contributes noticeably only at angles where the "ordinary" cross section is very small. In Paper I it was noted that the back-to-front ratio was smallest for hydrogen and increased progressively as the number of electrons in the target atoms was increased. A possible mechanism could be the ejection of two or more electrons from a single target atom. There is at present no adequate theory of this mechanism, but it would be logical to expect more events of this kind from targets containing more electrons.

III. IMPROVED QUANTUM-MECHANICAL METHODS

It was suggested by Oldham⁶ that the calculations in the forward direction could be improved by taking account of the influence of the projectile after the collision. This was done by Salin, ² who used the Born formalism but introduced an effective charge which depends on the velocities of the proton and ejected electron. The results of his treatment indicate that the Born cross sections are to be multiplied by the factor $2\pi\gamma/(1-e^{-2\pi\gamma})$, where $\gamma=|\vec{v}-\vec{k}|^{-1}-v^{-1}$, \vec{k} is the ejected-electron momentum (in atomic units), and \vec{v} is the proton velocity. Calculations

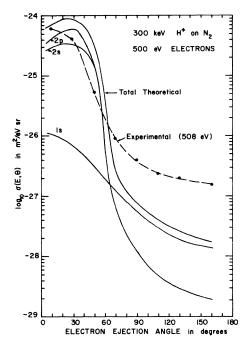


FIG. 3. Angular distribution of 500-eV electrons from nitrogen. Experimental values compared with Born calculations for three subshells.

using this factor are given in Figs. 4 and 5. A great improvement in the calculations for the forward direction is evident both for single- and multishell targets.

Macek³ approached the problem of the forward peak somewhat differently. Following a suggestion by one of the authors (MER) that the projectile may carry an electron along for a while before ejecting it, he treated it as a charge exchange into a continuum state of the projectile. To solve this threebody problem he used the Faddeev formulation7 of quantum mechanics in which all three bodies are treated on an equal basis. Selecting terms from the Neumann expansion of the Faddeev equations, Macek derived a formalism from which ddcs for electron ejection could be obtained. Calculations on this theory are also plotted in Figs. 4 and 5. Again, we have totaled the partial cross sections for each subshell after obtaining these by scaling from a hydrogenlike atom according to the binding energy.

Generally, Salin's theory is too low and Macek's results are too high but both match the shapes of the distributions somewhat better in the forward directions. Neither are any improvement on Born in the backward hemisphere. Both predict the previously noted hump in the 10° curves at an electron velocity equal to the projectile velocity, and both indicate that this hump is the start of a very large peak in the energy distribution which would appear at 0°. Experimental observation of this 0° peak has

recently been made in this laboratory by Crooks and Rudd, ⁸ thus providing convincing verification of the mechanism.

IV. BINARY-ENCOUNTER THEORY

Simultaneously with the development of quantum theories of ionization, a development has taken place in the use of the binary-encounter theory to describe this type of collision. The Gryzinski version of the theory has been used 5,10 to calculate energy distributions of ejected electrons integrated over all angles. Using a δ -function distribution of orbital velocities agreement was generally within a factor of 2. Gryzinski, however, has been criticized11,12 for his additional assumptions. Calculations without these assumptions were made by Gerjuoy¹³ and by Vriens. 14 The more general but cumbersome expressions of Gerjuov (somewhat simplified in the paper by Garcia¹⁵) reduce to those of Vriens when the assumption is made that the incident projectile has a mass large compared to that of the target electron. The resulting expressions had actually been worked out for this special case by Thomas. 16

The Thomas-Gerjuoy-Vriens equation for this case can be put into a convenient form by expressing it in terms of dimensionless quantities. Let m_1 be the mass and v_1 the velocity of the incident particle of charge Ze, let v_2 be the velocity, m_2 the mass, and E_2 the energy of the target electron before the

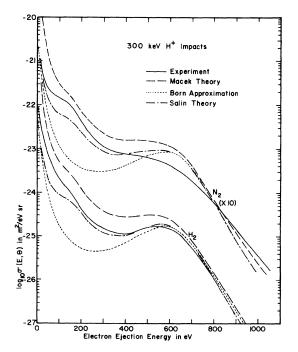


FIG. 4. Energy distribution of electrons ejected at 10° from hydrogen and from nitrogen. Experiment compared with Born, Macek, and Salin theoretical treatments.

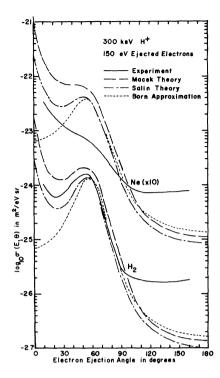


FIG. 5. Angular distribution of 150-eV electrons ejected from hydrogen and neon. Experiment compared with Born, Macek, and Salin theories.

collision, and let $U=\frac{1}{2}m_2v_0^2$ be the binding energy. ΔE is the energy transfer during the collision. Define the quantities $\phi=v_1/v_2$, $\delta=\Delta E/E_2$, and $u=U/E_2$, and let $\sigma_0=\pi(Ze^2/4\pi\epsilon_0)^2=6.51\times 10^{-18}Z^2m^2$ eV². Then the cross section for ionization with an energy transfer ΔE can be written

$$\begin{split} \sigma_{\Delta E} &= 0 \;, & \delta < u \;, \; \delta \geq \alpha \\ &= \sigma_A = \frac{\sigma_0}{\phi^2 \Delta E^3} \left(\; \delta + \frac{4}{3} \; \right) \;, & u \leq \delta \leq b \\ &= \sigma_B = \frac{\sigma_0}{\phi^2 \Delta E^3} \left(\; \frac{4}{3} \; \phi^3 - \frac{1}{6} \left[(\delta + 1)^{1/2} - 1 \right]^3 \right) \;, \\ & b \leq \delta \leq \alpha \end{split} \tag{1}$$

where $a=4 \phi^2+4\phi$ and $b=4\phi^2-4\phi$. The energy of the ejected electron is given by $E_{e,i}=\Delta E-U$.

Again using a δ -function orbital-velocity distribution, this equation yields differential cross sections within 75% of the experimental values over nearly the entire energy range for which experimental data are available. However, at some value of ejected-electron energy the calculated cross section drops abruptly to zero¹⁷ while the experimental values do not. This and other defects are eliminated by averaging the cross sections over a more realistic velocity distribution. If we let this distribution be $f(v_2)$, the average is calculated as follows:

$$\begin{split} \sigma_{\Delta E} &= \int_{0}^{v'} \sigma_{A}(v_{2}) f(v_{2}) \ dv_{2} + \int_{v'}^{\infty} \sigma_{B}(v_{2}) f(v_{2}) \ dv_{2} \ , \\ &\qquad \qquad U \leq \Delta E \leq 2 m_{2} v_{1}^{2} \\ &= \int_{-\infty}^{\infty} \sigma_{B}(v_{2}) f(v_{2}) \ dv_{2} \ , \qquad \Delta E \geq 2 m_{2} v_{1}^{2} \end{split} \tag{2}$$

where $v' = |\Delta E/2m_2v_1 - v_1|$.

Fock has derived¹⁸ the exact velocity distribution for electrons of any principal quantum number in the hydrogen atom. Letting q be the velocity associated with the average orbital energy \overline{E}_2 , the normalized distribution may be written $f(v_2) = 32q^5v_2^2/\pi(q^2+v_2^2)^4$. In hydrogen, $\overline{E}_2 = U$ and $q = v_0$, but this is not true in general. Other distributions have been investigated by Bonsen and Vriens. ¹⁹

Using this distribution, Garcia¹⁵ has performed the integration of Eq. (2) numerically. It may also be done analytically in closed form. The results of the integration are expressed in terms of the quantities

$$\alpha = \Delta E/\overline{E}_2$$
, $\Phi = v_1/q$, $\beta = \left(\frac{\alpha}{4\Phi} - \Phi\right)^2$.

The cross section is

$$\sigma_{\Delta E} = S_A + S_B$$
, $U \le \Delta E \le 2m_2 v_1^2$
= S_B , $\Delta E \ge 2m_2 v_1^2$ (3)

where

$$\begin{split} S_A &= \frac{\sigma_0}{\pi \Delta E^3 \Phi^2} \left(\frac{32 \beta^{3/2} \alpha}{3 (1+\beta)^3} + (\frac{4}{3} + \alpha) (\pi - 2R_1) \right) \;, \\ S_B &= \frac{\sigma_0}{\pi \Delta E^3 \Phi^2} \left[\; \frac{16}{3 (1+\beta)^3} \left(\frac{4}{3} \; \Phi^3 - \beta^{3/2} \; \alpha - \frac{\alpha (\alpha+\beta)^{3/2}}{1-\alpha} \right) \right. \\ &+ (\frac{4}{3} + \alpha) R_1 - \left(\frac{4}{3} - \frac{\alpha}{1-\alpha} \right) R_2 \; \right] \;, \end{split}$$

and

$$\begin{split} R_1 &= \tan^{-1}\beta^{-1/2} + \frac{\beta^{1/2}}{(1+\beta)^3} \left(1 + \frac{8}{3} \beta - \beta^2 \right), \\ R_2 &= R_3 + (1-\alpha)^{-3/2} \tan^{-1} \left(\frac{1-\alpha}{\alpha+\beta} \right)^{1/2}, \qquad \alpha < 1 \\ &= R_3 + (\alpha-1)^{-3/2} \ln \left(\frac{(\alpha+\beta)^{1/2} - (\alpha-1)^{1/2}}{(1+\beta)^{1/2}} \right), \quad \alpha > 1 \\ R_3 &= \left(2 + \frac{14}{3} \beta + \frac{8}{3} \alpha \right) \frac{(\alpha+\beta)^{1/2}}{(1+\beta)^3} - \frac{(\alpha+\beta)^{1/2}}{(1+\beta)(1-\alpha)}. \end{split}$$

At $\alpha = 1$, the expressions above converge to

$$\begin{split} S_B &= \frac{\sigma_0}{\pi \Delta E^3 \Phi^2} \left(\frac{16}{3(1+\beta)^3} \left[\frac{4}{3} \Phi^3 - \beta^{3/2} - \frac{4}{3} (1+\beta)^{3/2} \right. \right. \\ & \left. + \frac{3}{5} (1+\beta)^{1/2} \right] + \frac{7}{3} R_1 \right), \quad \alpha = 1 \ . \end{split}$$

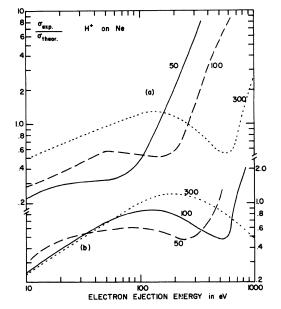


FIG. 6. Ratio of experimental to binary-encounter theoretical cross sections integrated over all angles.
(a) Average orbital energies for each target taken to be equal to the binding energies of each subshell. (b) Average orbital energies calculated from Slater's rules. Proton energies are in keV.

For targets with more than one electron shell, the binary-encounter theory can be used by adding the partial cross sections for each subshell, using the proper binding energy of each, as for the quantum theories. Garcia et al. 20 have done this for calculating total ionization cross sections, and it should also work for differential cross sections. Recent data taken by Toburen 21 at proton energies from 300 to 1700 keV with nitrogen as a target agree with the binary-encounter cross sections within a factor of 2.

The only parameter not well defined in the binary-encounter theory is the average orbital energy \overline{E}_2 . We define a ratio $\gamma = \overline{E}_2/U$ to facilitate the discussion. For hydrogen atoms $\gamma = 1$, and the virial theorem gives $\gamma = 1.6$ for helium, but for other atoms this quantity is not easily determinable. Robinson²² has suggested using Slater's screening rules to estimate this value for a given electron subshell. For helium, this yields 1.6 as before, but somewhat larger values are obtained for most other atoms. We have made computations both with $\gamma = 1$ and with γ determined by Slater's rules. In Fig. 1, both are shown in comparison with the Born calculations and experiment for 200-keV protons on nitrogen. One notes first that the binary-encounter theory with $\gamma = 1$ follows the Born curve quite closely even at fairly high energies, a result noted earlier. 17 Experiment seems to favor $\gamma = 1$ slightly, but to examine the question more

carefully, consider Fig. 6. This is a plot of the ratio of the experimental to the binary-encounter cross sections for neon at three proton energies. The top part of the graph is for $\gamma = 1$ and the bottom part for γ as given by Slater's rules. In the latter case, the actual values of γ used were 5.41, 1.50, and 1.47 for the 2p, 2s, and 1s subshells, respectively. The over-all improvement by using Slater's rules is evident, and also one sees that even though the low-energy region is not well described in either case, the curves are bunched more closely together using Slater's rules. Similar results are obtained for the other gases. The calculated values generally agree with experiment within a factor of 2, except at ejected-electron energies below 30 eV where theory is high.

Doubly differential cross sections have been calculated with the binary-encounter model by Bonsen and Vriens. ¹⁹ Their results are similar to those of the Born approximation at small and at intermediate angles. However, at large angles, owing to the neglect of the effect of the nucleus of the target, their cross sections are much too small.

V. CONCLUSIONS

A more complete picture of the process of electron production is now emerging. The well-known direct-impact mechanism in which energy is transferred from the incident projectile to an electron in the target, which then escapes in the field of the residual ion, is described by the Born approximation and somewhat less accurately by the binaryencounter theory. But even for an incident particle as simple as a proton there are additional mechanisms operating. Auto-ionization and Auger effects contribute appreciably to the ionization and cannot be neglected except for one-electron targets. Now another mechanism, charge transfer into continuum states, has been shown to be operating, and at least one additional mechanism is needed to explain all of the experimental results presented here.

For the single-shell targets, hydrogen, and helium, simple scaling has been shown to work quite well. This indicates that the ionization process is largely independent of the exact form of the wave function. However, for multishell atoms the scaling is too crude, and a better representation of the wave functions of such atoms is needed. The mechanism of charge transfer into continuum states explains the previous large discrepancy in the forward direction, but the formal theories agree only qualitatively with experiment, and an accurate quantitative treatment is still lacking.

While we now understand the mechanism of electron production at small and intermediate angles, there appears to be an as yet unknown mechanism operating which produces much larger than expected cross sections at large angles, especially with

multishell targets. We have speculated that this mechanism may be the simultaneous ejection of more than one electron from an atom.

For multishell atoms, both the Born and the binary-encounter theories yield reasonable energy distributions using simple scaling but the angular distributions are poorly described. Again, the Salin and Macek theories yield improved results

in the forward direction, but the agreement here is much less satisfactory than for single-shell atoms.

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Spectroscopy and Collisional Transfer in CH₃ Cl by Microwave-Laser Double Resonance

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The population changes in various rotation-vibration levels of CH₃Cl³⁵ were measured by microwave absorption in the presence of P(26) CO₂-laser radiation. The transition involved in the laser absorption was identified as ${}^{R}Q_{3}(6)$. The polarities, strengths, and relaxation times of the double-resonance signals on various microwave transitions were measured. These data were evaluated for information on collisional transfer between rotational levels, vibrational levels, and on the equalization of the rotational temperature between adjacent Jlevels. Collisional excitation of the isotopic species CH₃Cl³⁷ was observed. Vibrational relaxation from the $\nu_{\rm G}$ =1 state shows a smooth transition from diffusion to the walls at low pressure to thermal diffusion at high pressure. The conversion between ν_6 =1 and ν_3 =1 was shown to occur in either direction with a probability of about 1-in-300 per collision. The $\nu_{\rm g}=1$ vibrational satellite of the pure rotation spectrum in CH3Cl was shown to be irregular and the doubleresonance method was used to assign the transitions J_{5-6} , K=4, $\nu_6=1$ and J_{5-6} , K=l=+1, $\nu_6=1$.

I. INTRODUCTION

The coincidence in frequency between various lines of the CO2 laser with the rotation-vibration bands of several molecules opens the way for interesting spectroscopic measurements.

The laser radiation selectively transfers the population in specific rotational states from the vibrational ground state to vibrationally excited states. It is possible to determine the exact transitions by probing the participating rotational energy levels by means of microwaves while the laser is transmitted

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