



Technical Note

185

LECTURES ON ION-ATOM COLLISIONS

M. R. C. McDOWELL



**U. S. DEPARTMENT OF COMMERCE
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NATIONAL BUREAU OF STANDARDS

Technical Note 185

ISSUED MARCH 15, 1963

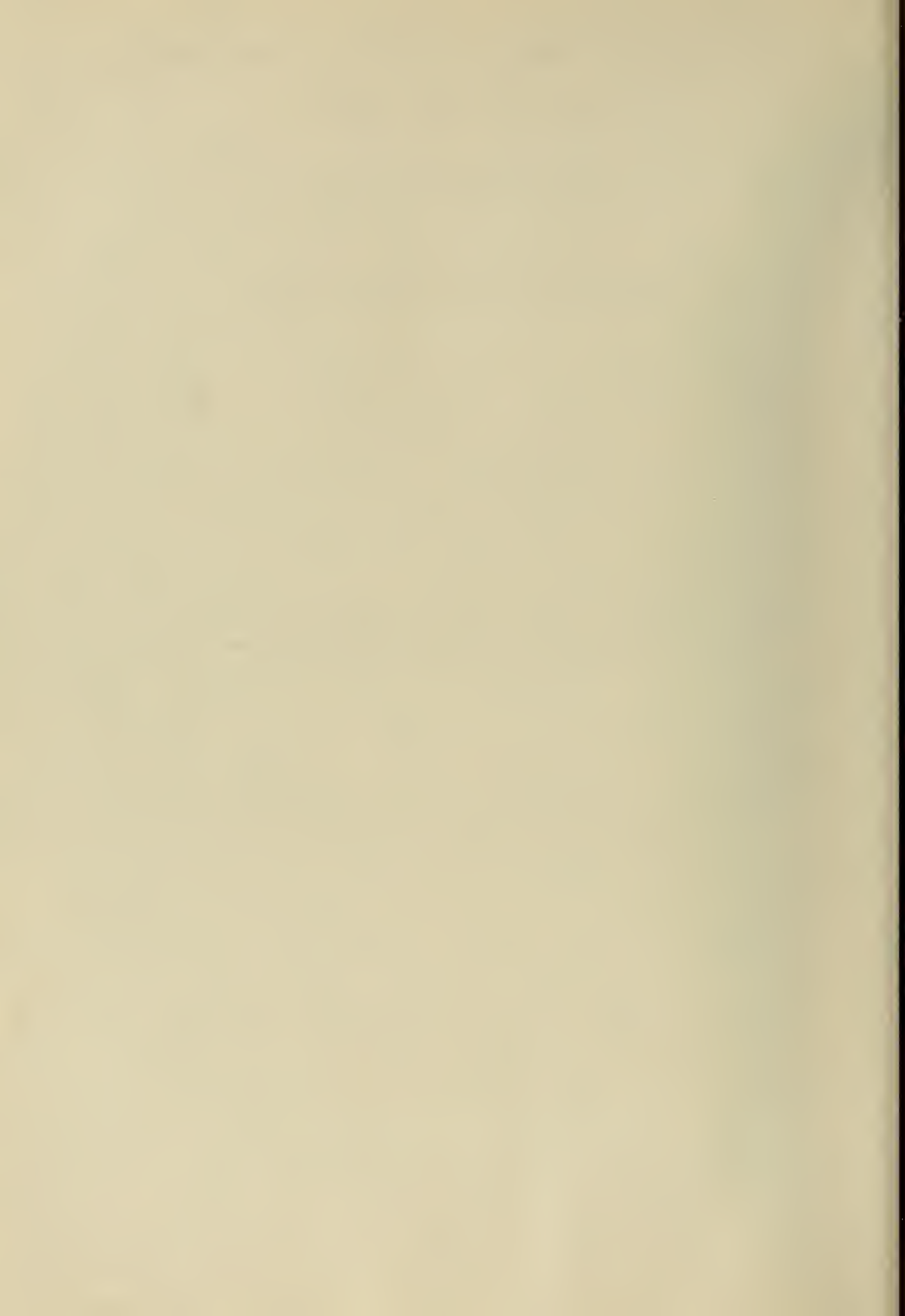
LECTURES ON ION-ATOM COLLISIONS

M. R. C. McDowell
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Lectures delivered at the Joint Institute for Laboratory Astrophysics, University of Colorado, during September, 1962.

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By

M. R. C. McDowell*

PREFACE

This report contains lectures delivered at the Joint Institute for Laboratory Astrophysics, University of Colorado, during September, 1962. The material of the first four is largely taken from recent books by D. R. Bates, and was presented for pedagogic purposes only. It does not purport, in any sense, to be a record of original work by the author. Any new material is confined to the last two lectures.

The numerical results quoted are taken, in part, from as yet unpublished work by M. B. McElroy (Belfast), Rudd and Jorgenson (University of Nebraska), and the author. Reference to this work should be made to the appropriate publication.

The author takes this opportunity of thanking the Bureau of Standards and the University of Colorado for their hospitality during this summer.

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Contents

	Page
Lecture I. The Impact Parameter Formulation of the Theory of Atom-Atom Collisions	1
Lecture II. Applications of the First Born Approximation. . .	12
Lecture III. Slow Charge Transfer.	22
Lecture IV. Charge Transfer in Other Cases.	34
Lecture V. (i) Further Remarks on Charge Transfer (ii) Curve - Crossing	44
Lecture VI. Ionization of Atomic Systems by Fast Protons. . .	56

LECTURE I

The Impact Parameter Formulation Of The Theory Of Atom-Atom Collisions

We will describe in this lecture the treatment of atom-atom (including ion-atom collisions) developed by Bates and his co-workers^(1 - 3) paying particular attention to the sequence of Born approximations and to the so called "distortion" approximation, but will leave to a later lecture any specific treatment of rearrangement collisions.

The theory to be described makes two basic assumptions.

(i) The relative motion of the colliding systems is sufficiently fast that the usual Born-Oppenheimer separation of electronic and nuclear motion is valid, and further, that the nuclear orbits are rectilinear, the velocity of relative motion \underline{v} being constant throughout the collision.

(ii) The velocity of relative motion $|\underline{v}|$ is sufficiently low that nuclear and relativistic effects may be ignored.

Assumption (i) (a), the Born-Oppenheimer separation, is valid at all energies of interest if both the systems are in S states, but may lead to serious errors at thermal velocities in other cases.

Assumption (ib), is equivalent to supposing that the de Broglie wave length λ of the incident particle, in the system in which the target is at rest, is small compared with atomic dimensions.

That is

$$\lambda = \frac{\hbar}{m_i v} \ll a_0 \quad (1.1)$$

For incident protons this is satisfied if $E_i < 10\text{ev}$, and for heavier atoms at correspondingly higher energies. However, even for atoms as heavy as Mercury, λ is $\sim 0.1 a_0$ at 300°K , so one should not suppose that cross sections calculated by the theory to be described are necessarily adequate at thermal energies, or that estimates of rate coefficients so obtained are applicable to upper atmospheric conditions.

Assumption (ii) is valid, insofar as relativistic effects are concerned, for heavy particle impact, up to several tens of Mev, provided inner shell electrons are ignored; but modification of the cross sections by the nuclear forces becomes important when $\lambda \sim 10^{-12}\text{cm}$. (If much of the contribution comes from small impact parameters), which is 10 Mev for H^+ impact, but correspondingly lower for heavier atoms. For example, $\lambda (\text{A}^+)$ is 10^{-12}cm at 100 kev. We can suppose that the limits of applicability of the theory are approximately

$$10\text{ ev} < E_i < 10\text{ Mev}$$

for H^+ impact.

We consider an unperturbed system, Hamiltonian H_0 , in an eigenstate Φ_s supposed known, with energy ϵ_s

$$H_0 \Phi_s = \epsilon_s \Phi_s \tag{1.2}$$

and suppose that the effect of the collision is to introduce a perturbation V , which is an implicit function of the time. Then the state of the system at time t may be described by a suitable

solution of

$$(H - i\frac{\partial}{\partial t}) \bar{\Psi}_n = 0 \quad (1.3)$$

where

$$H = H_0 + V \quad (1.4)$$

It is customary to expand $\bar{\Psi}_n$ in terms of the ϕ_s (all s)

$$\bar{\Psi}_n = \int_s a_{ns}(t) \phi_s e^{-iE_s t} \quad (1.5)$$

where $a_{ns}(t)$ are the occupation numbers of state s at time t , the system being originally in state n , and the collision taking place at impact parameter p . In particular one supposes the target to be at rest at the origin of co-ordinates in a frame $Oxyz$, and that the projectile moves with velocity \underline{v} parallel to and at a distance p from the z axis, the trace of its path in the xy plane at P being such that OP makes an angle $\bar{\phi}$ with the X axis. (Fig. I).

Then

$$X = p \cos \bar{\phi} ; Y = p \sin \bar{\phi} ; Z = vt \quad (1.6)$$

where $Z(p) = 0$.

FIGURE I.

(See Separate Sheet)

The probability that such a passage causes a transition from state n to state m is clearly $|a_{nm}(\infty)|^2$ and integrating over all impact parameters (supposing V independent of ϕ) the cross section is

$$Q_{nm}(\underline{E}) = 2\bar{u} \int_0^{\infty} |a_{nm}(\infty)|^2 p dp \quad (1.7)$$

Our aim, therefore, is to obtain an expression for $|a_{nm}(\infty)|^2$, and to evaluate it, for the particular transition of interest.

Let us substitute (1.5) in (1.3), making use of (1.2) to obtain

$$V \int_S a_{ns}(t) \phi_s e^{-iE_s t} = i \int_S \dot{a}_{ns}(t) \phi_s e^{-iE_s t}$$

and multiplying on the left by $\phi_m^* e^{iE_m t}$, integrate over all the electronic co-ordinates. We obtain

$$\int_S a_{ns}(t) V_{ms} e^{i\Delta E_{ms} t} = i \dot{a}_{nm}(t) \quad (1.8)$$

where

$$V_{ms} = \int \phi_m^* V \phi_s d\underline{r} \quad (1.9)$$

$$\Delta E_{ms} = E_m - E_s$$

This is a set of coupled integro-differential equn's, and does not admit of a general solⁿ.

Let us suppose

$$(i) \quad V_{nj} = 0 \quad ; \quad j \neq n \text{ or } m$$

and impose the boundary conditions

$$(ii) \quad a_{nn}(-\infty) = 1 \quad ; \quad a_{nm}(-\infty) = 0, \quad m \neq n.$$

(1.10)

In virtue of (i), (1.8) reduces to

$$i a'_{nm}(t) = a_{nn}(t) V_{mn} e^{i \Delta E_{mn} t} \quad (1.11)$$

If $m = n$, we may readily integrate this and obtain

$$a_{nn}(z) = 1 - \frac{i}{v} \int_{-\infty}^z V_{nn} dz' \quad (1.12)$$

where we have changed the variable for convenience. If now V_{nn} is small for all z , or if v is very large, we may take $a_{nn} \doteq 1$ (all z), and integrate (1.11) for $n \neq m$ to obtain

$$a_{nm}(z) = -\frac{i}{v} \int_{-\infty}^z V_{mn} e^{i \Delta E_{mn} z'/v} dz' \quad (1.13)$$

Thus, to this approximation, the cross section is

$$Q_{nm} = 2\bar{u} \int_0^{\infty} \frac{1}{v^2} \left| \int_{-\infty}^{+\infty} V_{mn} \exp \left\{ i \frac{\Delta E_{mn} z'}{v} \right\} dz' \right|^2 p dp \quad (1.14)$$

and is referred to as the 1st Born approximation since the assumptions made are mathematically equivalent to the usual wave formulation of the first Born approximation, when the nuclei are assumed to move as classical particles. A rigorous proof of the equivalence is provided by Frame (7).

This approximation is justified only if the sum of the transition probabilities remains small throughout the encounter

$$i.e. \quad \sum_p |a_{np}(z)|^2 \ll 1 \quad (1.15)$$

If this is not the case, improvements can be made in two directions. We can take specific account of those a_{np} judged to be most important, to a high order of approximation ("Distortion approximation"), or partial account of all of them (at least in principle) by a "2nd Born Approximation". In the latter, we start from (1.8) and use (1.12) and (1.13) on the R.H.S. This yields

$$i\nu \frac{\partial a_{nm}}{\partial z} = -\frac{i}{\nu} \int_{s \neq n} V_{ms} e^{i\varepsilon_{ms} z/\nu} \int_{-\infty}^z V_{ns} e^{i\varepsilon_{ns} z'/\nu} dz' + \left[1 - \frac{i}{\nu} \int_{-\infty}^z V_{nn} dz' \right] V_{nn} e^{i\varepsilon_{nn} z/\nu} \quad (1.16)$$

which may be written as

$$i\nu \frac{\partial a_{nm}}{\partial z} = (V_{nm} + W_{nm}) e^{i\varepsilon_{nm} z/\nu} \quad (1.17)$$

where

$$W_{nm} = -\frac{i}{\nu} \int_s V_{ms} e^{i\varepsilon_{ms} z/\nu} \int_{-\infty}^z V_{ns} e^{i\varepsilon_{ns} z'/\nu} dz' \quad (1.18)$$

As $\nu \rightarrow \infty$, the exponentials can be replaced by unity and

$$W_{nm} \doteq -\frac{i}{\nu} \int_s V_{ms} V_{ns} \doteq -\frac{1}{\nu} (V^2)_{nm}$$

which is of the second order in the interactions.

If we integrate (1.17), we have

$$a_{nm}(z) = \frac{i}{\nu} \int_{-\infty}^z (V_{nm} + W_{nm}) e^{i\varepsilon_{nm} z'/\nu} dz' \quad (1.19)$$

giving for the cross section

$$Q_{nm} = \frac{2\bar{u}}{v^2} \int_0^{\infty} \left| \int_{-\infty}^{+\infty} (V_{mn} + W_{mn}) e^{iE_{mn}z/v} dz \right|_p^2 dp \quad (1.20)$$

where the subscript 4 indicates that all terms of the 4th order in the interactions should be dropped, since further terms of this order arise from products of 3rd order and 1st order terms and these have not been included.⁽⁸⁾ In principle (1.20) takes proper account, to the third order in the interactions, of all the matrix elements, but in practice W_{mn} is approximated by a sum of what are considered the two or three most important matrix elements, including say V_{mm} and V_{mn} and terms differing from these only in magnetic quantum number.

The distortion approximation, on the other hand, begins by noting that of all the terms in (1.8), the only one whose magnitude is not affected by oscillatory factors is that involving V_{mm} , the so-called "secular" term. The distortion approximation takes this term almost completely into account.

We first of all remove the secular terms by writing

$$C_{ns} = a_{ns} \exp \left\{ i \int_0^t V_{ss} dt' \right\} \quad (1.21)$$

so that (1.8) is replaced by

$$i \dot{C}_{nm} = \sum_{s \neq m} C_{ns} V_{ms} \exp \left\{ -i \int_0^t \delta_{ms} dt' \right\} \quad (1.22)$$

with

$$\delta_{ms} = (\epsilon_m + V_{mm}) - (\epsilon_s + V_{ss}) \quad (1.23)$$

so that the resultant formulae are analogous to those of the 1st Born approximation, except that the unperturbed eigenenergies ϵ_s are replaced by the 1st order perturbed eigenenergies.

$$\eta_s = \epsilon_s + V_{ss} \quad (1.24)$$

Higher approximations may be obtained by retaining more than two terms in the initial expansions.

A very simple alternative derivation of (1.22) has been given by Bates (9). We start from (1.8) and the 1st Born solution for a_n . We have

$$\frac{\partial a_n}{\partial z} = \frac{1}{v} \int_s a_s(z) V_{ns} e^{-i\epsilon_{sn}z} \quad (1.8^1)$$

and suppose $a_s = 0$ ($s \neq n$) to obtain

$$\frac{\partial a_n}{\partial z} = \frac{1}{v} a_n V_{nn} \quad (1.25)$$

which integrates to give

$$a_n(z) = \exp \left\{ -\frac{i}{v} \int_0^z V_{nn} dz' \right\} \quad (1.26)$$

Now to obtain $a_m(z)$ we retain only a_m and a_n , so that (1.8¹)

becomes

$$i \frac{\partial a_m}{\partial z} = \frac{1}{v} \left\{ a_n(z) V_{nm} + a_m(z) V_{mm} \right\} \quad (1.27)$$

so using (1.26),

$$i \frac{\partial a_m}{\partial z} = \frac{i}{v} \left[a_m v_{mm} + v_{nm} \exp \left\{ -\frac{i}{v} \int_0^z v_{nn} dz' \right\} \right] \quad (1.28)$$

which may readily be integrated to yield

$$a_m(+\infty) = -\frac{i}{v} \int_{-\infty}^{+\infty} v_{nm} \exp \left\{ -\frac{i}{v} \epsilon_{nm} z - i\beta_{nm} \right\} dz \quad (1.29)$$

where

$$\beta_{nm} = \frac{i}{v} \int_0^z (v_{nn} - v_{mm}) dz' \quad (1.30)$$

Thus the cross section can be written

$$Q_{nm} = \frac{2\bar{u}}{v^2} \int_0^{\infty} \left| \int_{-\infty}^{+\infty} v_{nm} e^{-i\delta_{nm} z/v} dz \right|^2 p dp. \quad (1.31)$$

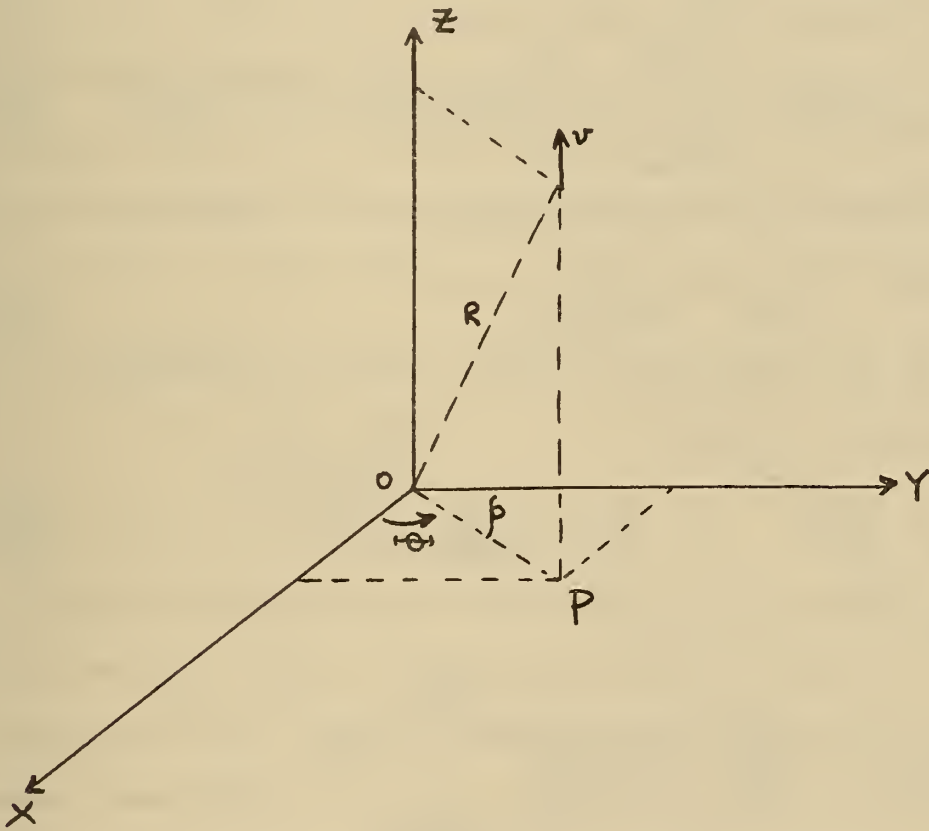
with γ_{mn} given by (1.23).

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FIG. 1

Coordinates used in the impact parameter formulation.



LECTURE II

Applications Of The First Born Approximation§ (1). The 1S-2S Excitation of H by H⁺: Impact Parameter Form

The cross section is given by

$$Q_{1s-2s}(\nu) = 2\pi \int_0^{\infty} |a_{1s,2s}(\infty)|^2 p dp \quad , \text{ units } a_0^2 \quad (2.1)$$

where we have seen (1.13) that

$$a_{1s,2s}(\infty) = -\frac{i}{\nu} \int_{-\infty}^{+\infty} V_{1s,2s} \exp\{i\Delta E_{1s,2s} z'/\nu\} dz' \quad (2.2)$$

Following Bates (1) we have that the interaction potential is

$$H' = \frac{1}{R} - \frac{1}{|\underline{r} - \underline{R}|} \quad (2.3)$$

where \underline{R} is the internuclear separation, and \underline{r} the electron's position vector. Taking

$$\phi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r} \quad ; \quad \phi_{2s} = \frac{1}{4\sqrt{2\pi}} (2-r) e^{-r/2} \quad (2.4)$$

we have

$$\begin{aligned} V_{1s,2s} &= -\frac{\sqrt{2}}{8\pi} \int \frac{(2-r)}{|\underline{r} - \underline{R}|} e^{-3r/2} d\underline{r} \\ &= -\frac{2\sqrt{2}}{27} (2+3R) e^{-3R/2} \end{aligned} \quad (2.5)$$

Using this in (2.2) and noting that it is an even function of Z , we have(1)

$$a_{1s,2s} = -\frac{2^{5/2}}{27\nu} \int_0^{\infty} (2+3R) e^{-3R/2} \cos\left(\frac{3z'}{8\nu}\right) dz' \quad (2.6)$$

which is the sum of two standard Fourier cosine transforms, and is equal to

$$a_{1s,2s} = \frac{2^{13/2} p^2 v}{9(1+16v^2)} K_2 \left\{ \frac{3\pm}{8v} (1+16v^2)^{1/2} \right\} \quad (2.7)$$

where $K_2(x)$ is the 2nd order modified Bessel function of the first kind, and the cross section may be readily evaluated numerically. The results are shown in Fig. (2.1). It may readily be seen that when v is large $\cos\left(\frac{3\pm}{8v}\right) \sim 1$, so that the cross section is proportional to v^{-2} . Further, when v is small the rapid oscillations of the cosine factor make the cross section go rapidly to zero with v . If we take $V_{1s,2s}$ to have range α , then $|a_{1s,2s}|^2$ is a maximum when

$$v \doteq \frac{E_{1s,2s} \alpha}{\lambda} \quad (2.8)$$

which is the usual adiabatic criteria.

Similar calculations have been carried out for transitions to the $2p_0$ and $2p_{\pm 1}$ states, and for these transitions when the incident particle is a hydrogen atom in the ground state, which remains unexcited⁽²⁾. The cross sections obtained are identical to these obtained earlier⁽³⁾ by the usual wave formulation. The collected results have been presented by Bates⁽⁴⁾. However, in the impact parameter formulation, the values of the transition probabilities allow one to make some estimate of their sum $\sum |a_{np}|^2$ at impact parameter p , and yield some information on the range of

validity of the Born approximation as a function of impact parameter. Since most of the contribution comes from small impact parameter. Bates (4) has evaluated

$$P' = \lim_{p \rightarrow 0} \sum_s' |a_{ws}|^2 \quad (2.9)$$

and considers the criterion $P' \ll 1$ satisfied if $P' < 0.15$, but grossly violated if $P' > 0.5$. For $[H^+, H(1S)]$ collisions he finds the Born approximation satisfactory (provided distortion is also unimportant) for $E_i > 200$ kev, and completely unreliable for $E_i < 50$ kev.

§(2). The Wave Formulation

Following Mott and Massey⁽⁵⁾ we have

$$Q_{nm}(v) = \frac{1}{2\pi v_n^2} \int_{k_{min}}^{k_{max}} |N_{nm}|^2 k dk \quad (2.10)$$

where

$$\underline{k} = \underline{k}_f - \underline{k}_i \quad (2.11)$$

and we may take

$$k_{min} \doteq \frac{E_{nm}}{v_n} \left\{ 1 + \frac{E_{nm}}{2\mu v^2} + \dots \right\} \quad (2.11)$$

and k_{max} as infinite. The interaction potential and the wave functions are identical to those given in §1. Substituting, and making use of Bethe's integral

$$\int \frac{e^{i\underline{k} \cdot (\underline{r} - \underline{R})}}{|\underline{r} - \underline{R}|} d\underline{r} = \frac{4\pi}{k^2} e^{i\underline{k} \cdot \underline{R}} \quad (2.12)$$

one obtains

$$Q_{nm}(v) = \frac{8}{S_i^2} \int_{k_{\min}}^{\infty} |\bar{I}_{nm}|^2 k^{-3} dk \quad (\bar{u} a_0^2) \quad (2.13)$$

where, in

$$Q_{nm}(v), \quad \bar{I}_{nm} = \int \chi_n^*(r) \chi_m(r) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (2.14)$$

and χ_n, χ_m are the initial and final atomic orbitals. For the $1s \rightarrow 2s$ transition this becomes,

$$\bar{I}_{nm} = \frac{\sqrt{2}}{8\pi} \int (2-r) e^{-3r/2} e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (2.15)$$

$$= \frac{\sqrt{2}}{2k} \int_0^{\infty} (2-r)r e^{-3r/2} \sin(kr) dr \quad (2.15)$$

which is readily evaluated by a suitable sequence of differentiations of

$$\int_0^{\infty} e^{-\alpha r} \frac{\cos(\beta r)}{\sin(\beta r)} = \frac{1}{(\alpha^2 + \beta^2)} \begin{cases} \alpha \\ \beta \end{cases} \quad (2.16)$$

to yield

$$\bar{I}_{1s,2s} = \frac{2^{17/2} k^2}{(4k^2 + 9)^3} \quad (2.17)$$

and the cross section may then be evaluated from (2.13) by numerical integration. The method may readily be generalized to collisions of a bare ion of charge Z_b incident on an ion isoelectronic with H of charge Z_a .

The resultant expression reduces⁽³⁾ at high energies to

$$Q_{1s,1s}(E_i) = \frac{11}{\alpha} \frac{Z_b^2}{Z_a^4} \left(1 - \frac{7.8}{\alpha}\right) \bar{n} a_0^2 \quad (2.18)$$

where $\alpha = E_i / M_b Z_a^2$

§(3). If the incident projectile is not a bare ion but another atomic system, a similar analysis shows that I_{nm} is replaced by a product of two factors, one being a matrix element for transitions of the target and one of the incident atom, these factors being identical to those in the single excitation case.

For

$$H(1s) + H(1s) \rightarrow H(nl) + H(n'l') \quad (2.19)$$

we have

$$Q_{1s \rightarrow nl, 1s \rightarrow n'l'} = \frac{8}{S_i^2} \int_{k_{min}}^{\infty} |\bar{I}(1s \rightarrow nl) \bar{I}(1s \rightarrow n'l')|^2 k^{-3} dk \quad (2.20)$$

At sufficiently high energies $k_{min} \rightarrow 0$, and sum rules may be applied to the matrix elements, to deduce the total cross section for all inelastic collisions⁽³⁾ (E_i in kev.),

$$Q(1s, 1s \rightarrow \Sigma, \Sigma) \doteq \frac{211}{E_i} (\bar{n} a_0^2) \quad (2.21)$$

where the major contribution comes from double ionization processes. Some representative results are shown in Fig. (2.2), and a table of the transitions for which results are available follows:

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FIG. 2.1. (From Bates 1961)

BORN & DISTORTION APPROXIMATIONS TO CROSS SECTIONS FOR



BATES, 1961.

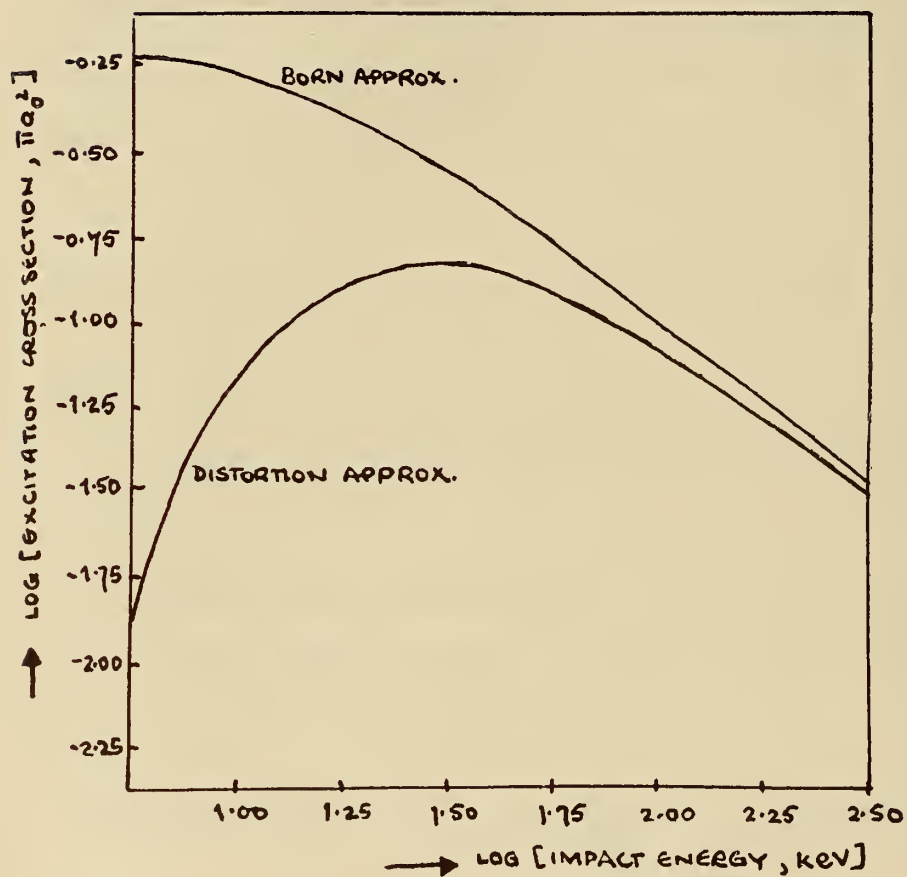


FIG. 2.2

FIRST BORN APPROXIMATION TO THE CROSS SECTION.

IMPACT ENERGY CURVES FOR:-



WHERE $n\ell$ REPRESENTS 2s, 2p, 3s, 3p, 3d or C.

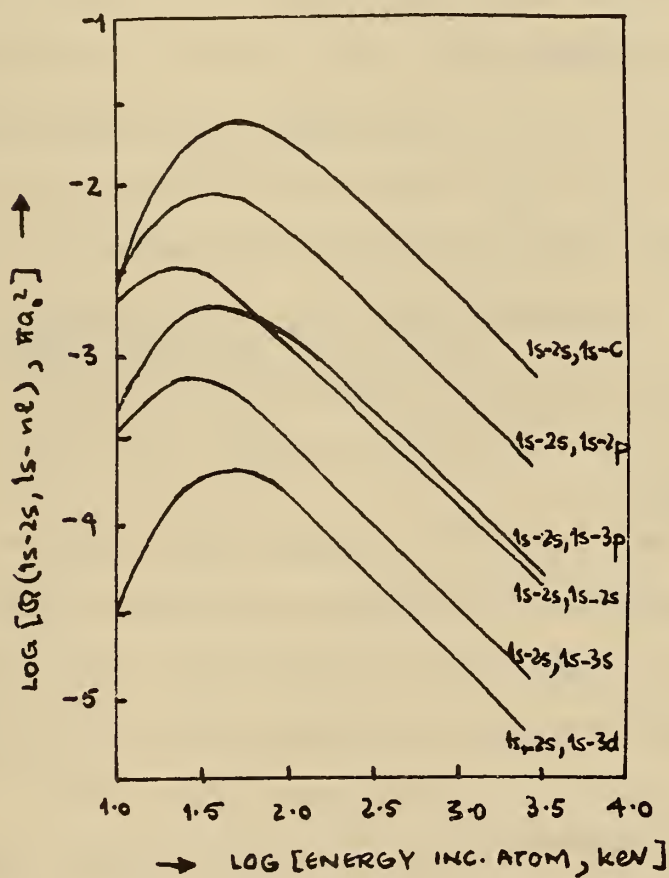


TABLE 2.1

A list of processes for which calculations have been carried out to the 1st Born approximation (not including charge transfer).

I. Proton Excitation

- 1) $H^+ + H(1s) \rightarrow H^+ + H(2s, 2p, 3s, 3p, 3d, C)$.
- 2) $H^+ + He(1s^2) \rightarrow H^+ + He(1s2p \text{ or } 1s3p' \text{ P})$.
- 3) $H^+ + Na(3s) \rightarrow H^+ + Na(3p)$.

II. Atom - Atom Excitation

- 4) $H(1s) + H(1s) \rightarrow H(1s, 2s, 2p, C) + H(2s, 2p, 3s, 3p, 3d, C)$
- 5) $H(1s) + He(1s^2) \rightarrow H(\Sigma) + He(1s2p' \text{ P})$
- 5¹) $He^+(1s) + He(1s^2) \rightarrow He^+(\Sigma) + He(1s2p' \text{ P})$
- 6) $H(1s) + He(2s^3S) \rightarrow H(\Sigma) + He(2p \text{ or } 3p^3P)$
 $Ne(1s) + He(2s^3S) \rightarrow Ne(\Sigma) + He(2p \text{ or } 3p^3P)$

III. Ionization

- 7) $H^+ \text{ (or } He^{++}) + He \rightarrow H^+ \text{ (or } He^{++}) + He^+(1s) + e$
- 8) $H^+ + He(1s^2) \rightarrow H^+ + He^+(2s, 2p, 3p, 3d) + e$
- 9) $H^+ + Li(1s^2 2s) \rightarrow H^+ + Li^+(1s^2) + e$
- 10) $H^+ + Ne \rightarrow H^+ + Ne^+ + e$

IV. Double Ionization

- 11) $He^+(1s) + H(1s) \rightarrow He^{++} + H(\Sigma) + e$
- 12) $He(1s^2) + H(1s) \rightarrow He(\Sigma) + H^+ + e$

TABLE 2.1 (Con't.)

V. Electron Loss

- 13) $H(1s) + H^{-}(1s^2) \rightarrow H(1s \text{ or } 2p) + H(1s \text{ or } 2p) + e$
- 14) $He(1s^2) + H^{-}(1s^2) \rightarrow He(1s^2) + H(1s) + e$

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LECTURE III

Slow Charge Transfer§1. The Adiabatic Approximation

We suppose that below the maximum predicted by the adiabatic hypothesis that the projectile and the target particle may be considered as forming a quasi-molecule, the velocity of relative motion being such that the electron, considered as a classical particle, would complete several orbits while the nuclear separation changed inappreciably. Then we consider that the quasi-molecule makes transitions (infrequently; $a_{ns} \ll 1$, all s) under the perturbation of the relative motion.

Let the total Hamiltonian be

$$H = H_0 + V(\underline{r}, \underline{R}) \quad (3.1)$$

so the system is described by a state function Ψ_n satisfying

$$(H - i \frac{\partial}{\partial t}) \Psi_n(\underline{R}, \underline{r}) = 0 \quad (3.2)$$

Now at some fixed R , the quasi-molecule has eigen states $\chi_s(\underline{R}, \underline{r})$ with eigen energies $\epsilon_s(R)$ such that

$$H \chi_s(\underline{R}, \underline{r}) = E_s \chi_s(\underline{R}, \underline{r}). \quad (3.3)$$

Then expand

$$\Psi_n = \int_S C_{ns}(t) \chi_s(\underline{r}, \underline{R}) \exp \left\{ -i \int^t E_s(R) dt' \right\} \quad (3.4)$$

and substitute (4) in (2). We obtain

$$\begin{aligned}
 H \int_S C_{ns} \chi_s \exp \left\{ -i \int^t E_s dt' \right\} &= i \int_S C_{ns} \chi_s \exp \left\{ -i \int^t E_s dt' \right\} \\
 &+ \int_S C_{ns} \chi_s E_s \exp \left\{ -i \int^t E_s dt' \right\} \\
 &+ i \int_S C_{ns} \frac{\partial \chi_s}{\partial t} \exp \left\{ -i \int^t E_s dt' \right\}
 \end{aligned} \tag{3.5}$$

Multiply on the left by

$$\chi_m^* \exp \left\{ +i \int^t E_m dt' \right\}$$

and integrate over the electron coordinates, assuming that

$$\int \chi_s \chi_m^* \exp \left\{ i \int^t \Delta E_{ms} dt' \right\} d\mathbf{r} = \delta_{ms} \tag{3.6}$$

to obtain

$$\dot{C}_{nm} = - \int_S C_{ns} \langle m | \frac{\partial}{\partial t} | s \rangle \exp \left\{ -i \int^t \Delta E_{sm} dt' \right\} \tag{3.7}$$

Now

$$\frac{\partial \chi_s(\underline{R}, t)}{\partial t} = \frac{\partial \chi_s}{\partial \underline{R}} \cdot \frac{\partial \underline{R}}{\partial t} \tag{3.8}$$

so (3.7) may be written

$$\dot{C}_{nm} = - \underline{v} \cdot \int_S C_{ns}(t) \langle m | \nabla_R | s \rangle \exp \left\{ -i \int^t \Delta E_{sm} dt' \right\} \tag{3.9}$$

which is the P.S.S. approximation in its simplest form.

[Choosing the (arbitrary)⁽¹⁾ phase of $\chi_s(\underline{r}, \underline{R})$ such that

$$\frac{\chi_s - \chi_s^*}{\chi_s + \chi_s^*} = f(\underline{r}) \quad \text{only}$$

and using the result $\nabla_R \int \chi_s^* \chi_s dr \equiv 0$, we have

$$\langle s | \nabla_R | s \rangle = 0 \quad (3.10)$$

Now suppose that

$$C_{ns}(-\infty) = \delta_{ns} \quad (3.11)$$

as our boundary condition, and assume that we can put $C_{ns}(t) = C_{ns}(-\infty)$ on the r.h.s. of (3.9). Then we obtain the uncoupled equation,⁽²⁾

$$\dot{C}_{nm} = -\underline{v} \cdot \langle m | \nabla_R | n \rangle \exp\left\{-i \int^t \Delta E_{mn} dt'\right\} \quad (3.12)$$

which may be integrated to yield

$$C_{nm}(+\infty) = - \int_{-\infty}^{+\infty} \underline{v} \cdot \langle m | \nabla_R | n \rangle \exp\left\{-i \int^t \Delta E_{mn} dt'\right\} dt \quad (3.13)$$

and

$$Q_{nm} = 2\bar{u} \int_0^{\infty} |C_{nm}(t)|^2 \not{p} dp \quad (3.14)$$

These equations are appropriate only in the absence of coupling, and even the coupled equations (3.9) are inappropriate if cond. (3.6) is not satisfied. In the limit of high velocities we may obtain the impact parameter version of the first Born from this by

using 1st order perturbed eigenfunctions on (3.13) and the unperturbed eigenenergies.

§ 2. Charge Transfer

We now consider the process



in which an electron is transferred from state n of B to state m of A . We deal first with the symmetric resonance case in which

$$A \rightleftharpoons B, \quad m = n. \quad (3.2.2)$$

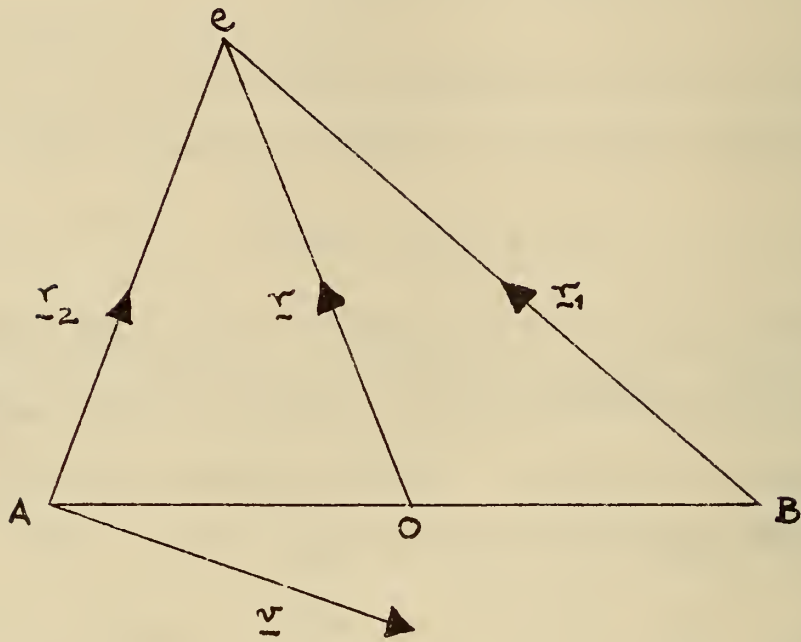
If the atom $(B+e)$ is in state ϕ_s as $R \rightarrow \infty$ the corresponding molecular eigenfunctions are $\chi_s^+, -$, even and odd with respect to interchange of the nuclei. The corresponding L.C.A.O. approximations to the total state function are

$$\Psi_{1,2} = \frac{1}{\sqrt{2}} [\chi_s^+ \pm \chi_s^-] \quad (3.2.3)$$

where Ψ_1 corresponds to the electron on nucleus B as $R \rightarrow \infty$, Ψ_2 to nucleus A . Adopting the co-ords. shown in Fig. 3.1

FIG. 3.1

Co-ordinates For The Exchange Problem



and letting $Z = vt$ determine the origin of t , we have⁽³⁾

$$Z - vt = z_1 - z - \frac{1}{2}Z = z_2 - z + \frac{1}{2}Z = 0 \quad (3.2.4)$$

We now choose an expansion^(1,2)

$$\Psi = \int_S C_S^+ X_S^+ + C_S^- X_S^- \quad (3.2.5)$$

where

$$X_S^\pm = \left\{ (X_S^+ + X_S^-) e^{-ikz/2} \pm (X_S^+ - X_S^-) e^{+ikz/2} \right\} \cdot \exp \left\{ -i \int^t (\mathcal{E}_S^\pm + \frac{1}{8}mv^2) dt' \right\} \quad (3.2.6)$$

Then

$$(H - i\frac{\partial}{\partial t}) X_S^\pm = i \left\{ \begin{array}{l} \pm (\mathcal{E}_S^+ - \mathcal{E}_S^-) X_S^\pm \sin(\frac{1}{2}kz) \\ -\frac{1}{2}v \left[\frac{\partial}{\partial z_{\tau_1}} (X_S^+ + X_S^-) e^{-ikz/2} \pm \frac{\partial}{\partial z_{\tau_2}} (X_S^+ - X_S^-) e^{+ikz/2} \right] \end{array} \right\} \cdot \exp \left\{ -i \int^t (\mathcal{E}_S^\pm + \frac{1}{8}mv^2) dt' \right\} \quad (3.2.7)$$

such that

$$(H - i\frac{\partial}{\partial t}) X_S^\pm = 0 \quad \text{when } \underline{v} = 0 \text{ for all } R, \\ \text{or when } R \rightarrow \infty \text{ for all } \underline{v}$$

[To prove this note that

$$H X_S^\pm = \mathcal{E}_S^\pm X_S^\pm$$

and that

$$H e^{\pm ikz/2} = \frac{1}{8}mv^2 e^{\pm ikz/2}$$

].

We now impose the boundary conditions

$$C_n^\pm(-\infty) = \frac{1}{\sqrt{2}} ; C_s^\pm(-\infty) = 0, \quad s \neq n$$

and make the assumption that transitions are infrequent

$$C_{s \neq n}^\pm(t) \doteq 0 \quad (3.2.8)$$

Then from

$$(H - i\frac{\partial}{\partial t}) \psi = 0 \quad (3.2.9)$$

we have

$$\begin{aligned} i \sum_s \dot{C}_s^+ \int (X_j^+)^* X_s^+ dr + i \sum_s \dot{C}_s^- \int (X_j^+)^* X_s^- dr \\ = C_j^+ T_j^+ \end{aligned} \quad (3.2.10)$$

where

$$T_j^+ = \int (X_j^+)^* [H - i\frac{\partial}{\partial t}] X_j^+ dr \quad (3.2.11)$$

Clearly

$$\int (X_j^+)^* (X_s^-) dr = 0, \quad \text{all } s \quad (3.2.12)$$

and if we further assume (incorrectly) [equiv. to assuming

$$C_s^+ = 0, \quad s \neq j]$$

$$\int (X_j^+)^* X_s^+ dr = \delta_{js} N_{js}^+ \quad (3.2.13)$$

we obtain

$$i \dot{C}_j^+ = (N_{jj}^+)^{-1} C_j^+ T_j^+ \quad (3.2.14)$$

Now

$$N_{jj}^+ = 1 + \sigma_{jj}^+ + \frac{1}{2} i \int \{ \chi_i^{-*} \chi_j^+ - \chi_j^{+*} \chi_i^- \} \sin v z \, dz \quad (3.2.15)$$

The last term of this equation vanishes by symmetry arguments to leave the Bates - McCarroll result

$$i \dot{C}_j^+ = c_j^+ T_j^+ / (1 + \sigma_j^+)$$

$$\sigma_j^+ = \frac{1}{2} \int (\chi_j^{+*} \chi_j^+ - \chi_j^{-*} \chi_j^-) \cos v z \, dz \quad (3.2.16)$$

Retaining only the symmetric part of T_j^+ one may then integrate this to get the transfer probability in the form.

$$P = \sin^2 \Xi(p) \quad (3.2.17)$$

where

$$\Xi(p) = \frac{1}{2} [(\beta^- - \beta^+) + \frac{1}{v} \int_{-\infty}^{+\infty} \Delta \epsilon_n^{+i-} \, dz] \quad (3.2.18)$$

and

$$\beta^\pm = -\frac{1}{v} \int_{-\infty}^{+\infty} \{ T_{\text{sym}}^\pm / (1 \pm \sigma) \} \, dz \quad (3.2.19)$$

If v is small, so is $(\beta^- - \beta^+)$, and the result reduces to the P.S.S. method. In general, the effect of the $(\beta^- - \beta^+)$ term is to reduce the cross section below the P.S.S. value. For the resonant H^+ on H case, the effect is noticeable at 2 keV, and significant above 25 keV.^(4,5) Excellent agreement with the experimental results of Fite et al.⁽⁶⁾ is obtained by normalizing

Fite's result to the theoretical value at the lowest measured energy. Above 15 kev Ferguson's calculations give a result decreasing much more rapidly than the experimental values, but inclusion of coupling to the 2p state⁽⁷⁾ gives a marked improvement (Fig. 3.2).

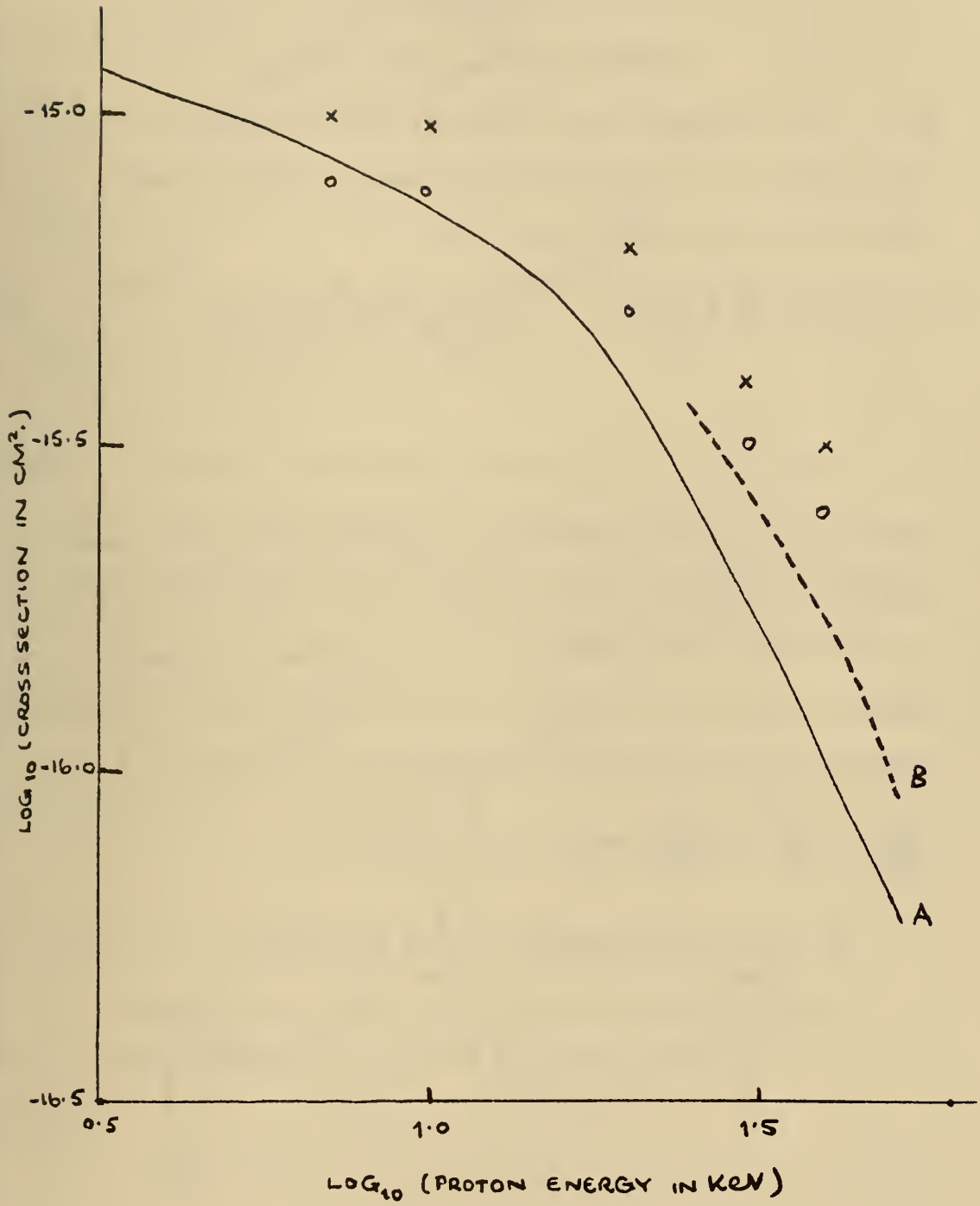
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CAPTION TO FIGURE 3.2

The solid curve shows Ferguson's calculated values of Q^{trans} for H^+ in H, the dashed curve the effect of including coupling to 2p. (McElroy 1962). The x's are the experimental points renormalized (o's) to the P.S.S. calculation at 1 kev.

FIG. 3.2



LECTURE IV

Charge Transfer In Other Cases

§1. The treatment given in Lecture III can readily be generalized to take account of non-symmetric charge transfer.

Expanding the total wave function as

$$\Psi_n = \sum_p a_p(t) \phi_p^A \left(\frac{r}{R} \right) e^{-i \int^t \eta_p dt'} + \sum_q b_q(t) \phi_q^B \left(\frac{r}{R} \right) e^{-i \int^t \eta_q dt'} \quad (4.1)$$

where ϕ_p^A , ϕ_q^B are proportional to eigenfunctions of the quasi-molecule AB with the active electron on A or B respectively when $R \rightarrow \infty$. Noting that ϕ_p^A and ϕ_q^B are not in general orthogonal (in the absence of exact wave functions) one can derive a set of differential equations for the occupation coefficients of the form⁽¹⁾

$$\begin{aligned} \frac{\partial a_i}{\partial z} + \sum_q S_{iq} \frac{\partial b_q}{\partial z} \exp \left\{ -\frac{i}{v} \int_{-\infty}^z \Delta \eta_{iq} dz' \right\} \\ = - \sum_{p \neq i} a_p L_{ip} \exp \left\{ -\frac{i}{v} \int_{-\infty}^z \Delta \eta_{pi} dz' \right\} \\ - \sum_q b_q M_{iq} \exp \left\{ \frac{i}{2} v z - \frac{i}{v} \int_{-\infty}^z \Delta \eta_{qi} dz' \right\} \end{aligned} \quad (4.2)$$

together with similar equations for the b_j , where

$$\begin{aligned}
 S_{iq} &= \int \chi_i^{A*} \chi_q^B e^{i\nu z} \underline{dr} & \} \\
 L_{ip} &= \int \chi_i^{A*} \nabla_{\underline{r}_1} \chi_p^A \underline{dr} & \} \\
 M_{iq} &= \int \chi_i^{A*} \nabla_{\underline{r}_2} \chi_p^B e^{i\nu z_2} \underline{dr} & \} \quad (4.3)
 \end{aligned}$$

and

$$\phi_p^A = \chi_p^A e^{-\frac{1}{2}\nu z} e^{-\frac{i}{\theta}\nu^2 t} \quad (4.4)$$

Clearly the coupling terms involving the M_{iq} are of considerable importance. This set of equations has so far proved intractable.

A two state approximation which should be valid at somewhat higher energies has been developed by several authors, ^(1,2,3,4) and will now be described. We expand ⁽¹⁾

$$\bar{\Psi}_n = a_i \psi_i^A(\underline{r}) e^{-i\varepsilon_i^A t} + b_j \psi_j^B(\underline{r}) e^{-i\varepsilon_j^B t} + \gamma(\underline{r}, t) \quad (4.5)$$

where $\gamma(\underline{r}, t)$ is orthogonal to both the a_i and b_j term and the

ψ_i^A, ψ_i^B are proportional to the initial and final unperturbed atomic eigenfunctions. Now

$$(H - i\frac{\partial}{\partial t}) \bar{\Psi}_n = 0 \quad (4.6)$$

so substituting (4.5) we get a set of coupled equations

$$i \{ \dot{a}_i + b_j S_{ij} e^{-i\Delta E_{ij}t} \} = b_j k_{ij} e^{-i\Delta E_{ij}t} + \sum_p a_p H_{ip} e^{-i\Delta E_{ip}t}$$

$$i \{ \dot{b}_j + a_i S_{ji} e^{-i\Delta E_{ij}t} \} = a_i k_{ji} e^{-i\Delta E_{ij}t} + \sum_q b_q H_{jq} e^{-i\Delta E_{jq}t} \quad (4.7)$$

with

$$S_{ij} = \int \phi_i^{A*}(\underline{r}_1) \phi_j^B(\underline{r}_2) e^{i\nu z} d\underline{r} \quad \}$$

$$k_{ij} = \int \phi_i^{A*}(\underline{r}_1) V^A(\underline{r}_1) \phi_j^B(\underline{r}_2) e^{i\nu z} d\underline{r} \quad \}$$

$$H_{ij} = \int \phi_i^{A*}(\underline{r}_1) V^B(\underline{r}_2) \phi_j^A(\underline{r}_1) d\underline{r} \quad \} \quad (4.8)$$

and V^A, V^B are the initial and final unperturbed potentials.

We have taken the atomic eigenfunctions to be

ϕ_i^A and ϕ_j^B , where

$$\psi_i^A = \phi_i^A \exp \left\{ -\frac{i}{2} \nu z - \frac{i}{8} \nu^2 t \right\} \quad \}$$

$$\psi_j^B = \phi_j^B \exp \left\{ \frac{i}{2} \nu z - \frac{i}{8} \nu^2 t \right\} \quad \} \quad (4.9)$$

Making the usual two state approximation

$$a_i(-\infty) = 1 ; a_j(-\infty) = b_j(-\infty) = 0 \quad (j \neq i) \quad (4.10)$$

and assuming transitions are rare, gives

$$i \{ \dot{a}_i + b_j S_{ij} e^{-i\Delta E_{ij}t} \} = b_j k_{ij} e^{-i\Delta E_{ij}t} + a_i H_{ii} \quad (4.11a)$$

$$i \{ \dot{b}_j + a_i S_{ji} e^{-i\Delta E_{ij}t} \} = a_i k_{ji} e^{-i\Delta E_{ij}t} + b_j H_{jj} \quad (4.11b)$$

Multiplying the lower equation by $S_{ij} e^{-i\Delta\epsilon_{ji}t}$ on the right, and subtracting

$$i\{1 - |S_{ij}|^2\} a_i = a_i (H_{ii} - S_{ij} k_{ji}) + b_j (k_{ji} - S_{ij} H_{jj}) e^{-i\Delta\epsilon_{ji}t} \quad (4.12a)$$

and similarly

$$i\{1 - |S_{ij}|^2\} b_j = b_j (H_{jj} - S_{ji} k_{ij}) + a_i (k_{ij} - S_{ji} H_{ii}) e^{-i\Delta\epsilon_{ij}t} \quad (4.12b)$$

If we note that the imaginary parts of

$$\alpha_i = \frac{H_{ii} - S_{ij} k_{ji}}{1 - |S_{ij}|^2} \quad ; \quad \beta_j = \frac{H_{jj} - S_{ji} k_{ij}}{1 - |S_{ij}|^2} \quad (4.13)$$

are anti-symmetric in t , we may remove the secular terms by putting

$$a_i = a_i^0 e^{-\int_{-\infty}^t \alpha_i dt'} \quad ; \quad b_j = b_j^0 e^{-\int_{-\infty}^t \beta_j dt'} \quad (4.14)$$

to obtain

$$i a_i^0 = b_j^0 \left[\frac{k_{ji} - S_{ij} H_{jj}}{1 - |S_{ij}|^2} \right] \exp \left[-i\Delta\epsilon_{ji}t + i\delta_{ij} \right] \quad (4.15a)$$

$$i b_j^0 = a_i^0 \left[\frac{k_{ij} - S_{ji} H_{ii}}{1 - |S_{ij}|^2} \right] \exp \left[-i\Delta\epsilon_{ij}t - i\delta_{ij} \right] \quad (4.15b)$$

where

$$\delta_{ij} \equiv \int_{-\infty}^t (H_{ii} - H_{jj}) dt' \quad (4.16)$$

and makes allowance for distortion. In the symmetric resonance case

$\delta_{ij} \equiv 0$, and the equations uncouple to give (5)

$$Q = 2\bar{u} \int_0^{\infty} |b_j(\infty)|^2 \phi \, d\phi \quad (4.17)$$

where

$$|b_j(\infty)|^2 = \sin^2 \left\{ \int_{-\infty}^{+\infty} M_{ij} \, dt \right\} \quad (4.18)$$

and

$$M_{ij} = \left[\frac{k_{ji} - \delta_{ji} H_{ii}}{1 - |S_{ij}|^2} \right] \exp\{-i\Delta E_{ij}t\} \quad (4.19)$$

However, we must generally make the simplifying assumption

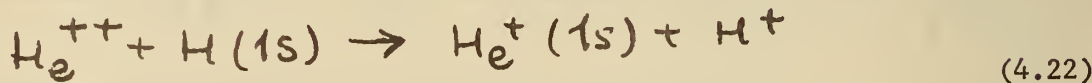
$b_j(t) \ll a_i(t)$ (all t), and we then obtain

$$|b_j(\infty)|^2 = \left| \int_{-\infty}^{+\infty} M'_{ij} \, dt \right|^2 \quad (4.20)$$

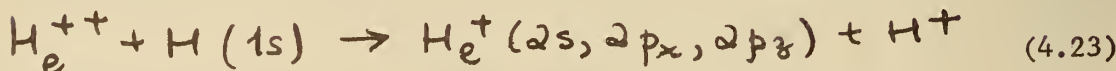
with

$$M'_{ij} = M_{ij} e^{-i\delta_{ij}} \quad (4.21)$$

These equations have been applied to



by McCarroll and McElroy⁽⁶⁾ and to



by McElroy⁽⁷⁾ and the results are tabulated below. The agreement with the results of Fite et al.⁽⁸⁾ and the data taken in molecular hydrogen⁽⁹⁾ is shown in Fig. 4.1. It is far from clear whether

Bates and Lynn's⁽¹⁰⁾ prediction of a rapid decrease in the cross section for the accidental resonance case as $v \rightarrow 0$ is confirmed. Probably coupling is at least as important an effect as distortion.

Equations (4.15) reduce to those of Bassel and Gerjnoj⁽¹¹⁾ if the $|S_{ij}|^2$ term is omitted.

§2. Comparison of the Various Treatments

If in the result (3.38) we ignore the $\beta \pm$ term, then the P.S.S. approximation yields for the cross section for symmetric resonance charge transfer

$$Q = 2\bar{u} \int_0^{\infty} p \sin^2 \xi(p) dp \quad (1)$$

with

$$\xi = \xi_0 = \frac{1}{v} \int_0^{\infty} \frac{\Delta E^{+,-}(R) R dR}{(R^2 - p^2)^{1/2}} \quad (2)$$

Similarly (4.18) yields

$$\xi = \xi_1 = \int_{-\infty}^{+\infty} \frac{(K_{ij} - S_{ij} H_{jj}) dt}{(1 - |S_{ij}|^2)} \quad (3)$$

If we ignore the e^{-ivz} term ($v \rightarrow 0$) and take $|S_{ij}|^2 \ll 1$, we have

$$\xi_1 \doteq \frac{1}{v} \int_0^{\infty} \frac{(K_{ij} - H_{jj}) R dR}{(R^2 - p^2)^{1/2}} \quad (4)$$

and

$$K_{ij} - H_{jj} \doteq \langle A | V^A | B \rangle - \langle A | V^B | A \rangle \quad (5)$$

which differs from (2) only in that the molecular eigenenergies

are replaced by their L.C.A.O. approximations. Result (3) in the limit $e^{-ivz} \rightarrow 1$ has been obtained in a simple fashion by Gurnee and Magee⁽²⁾ and their method has recently been extended to the asymmetric case by Rapp and Francis⁽⁴⁾, who ignore the exponential in (4.9). They show that in this approximation asymmetric resonance charge transfer should show the typical

$$\sqrt{Q} = A \log E + B$$

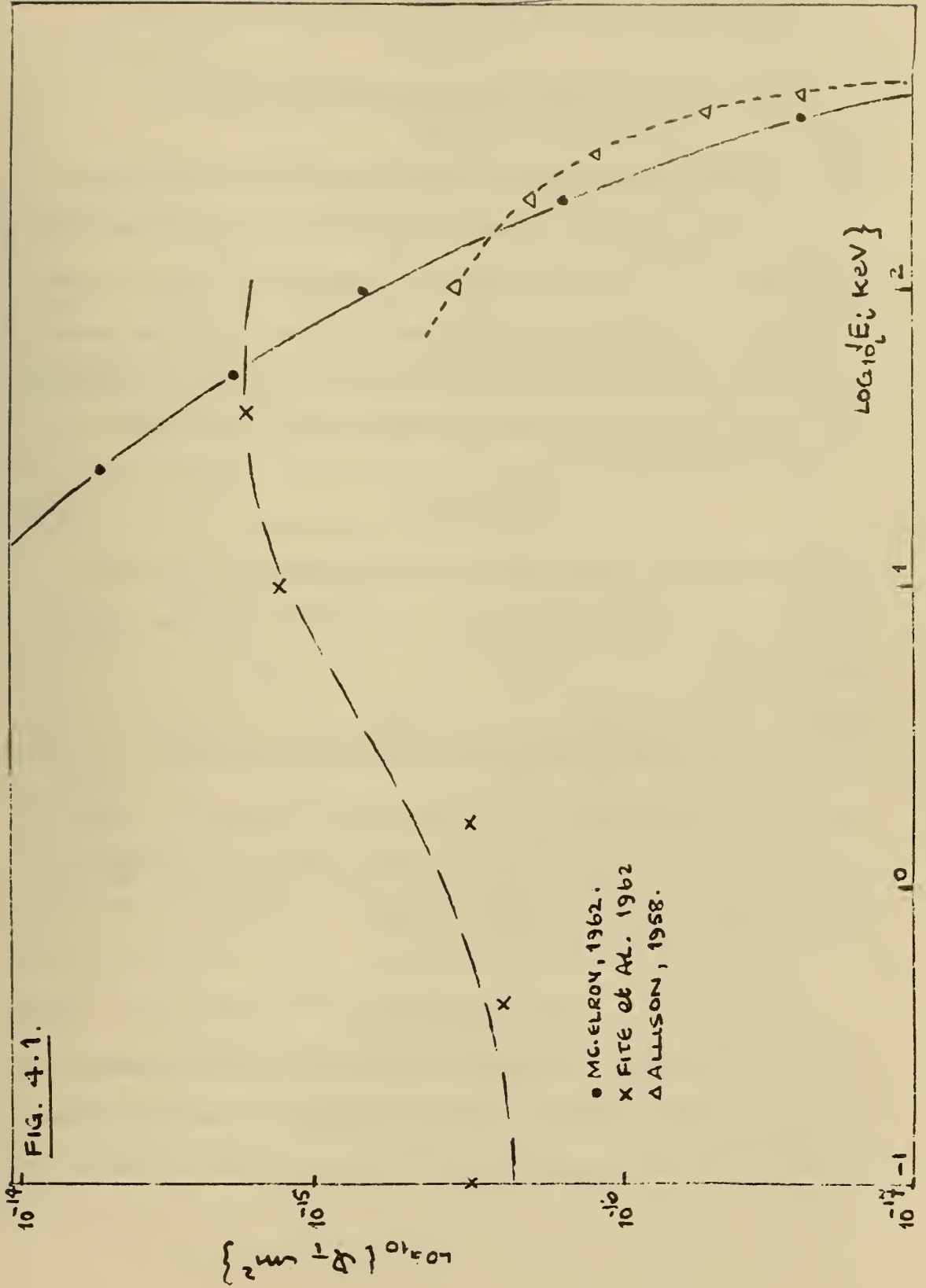
behavior down to some minimum energy E_0 which depends on the energy to defect ΔE_{if} in a complicated fashion. For $E < E_0$, the usual adiabatic variation of the cross section is obtained.

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ELECTRON CAPTURE CROSS-SECTIONS (UNITS cm^2) FOR α PARTICLES IN H
[MCCLELLY, 1962]

IMPACT ENERGY	25 keV	50 keV	100 keV	200 keV	400 keV	800 keV
Q_0 (1s)	2.21×10^{-17}	5.65×10^{-17}	5.96×10^{-17}	3.01×10^{-17}	1.31×10^{-17}	2.34×10^{-18}
Q_1 (1s)	1.06×10^{-14}	1.23×10^{-17}	1.26×10^{-17}	1.01×10^{-17}	5.44×10^{-18}	1.47×10^{-18}
Q_2 (2s)	3.50×10^{-16}	2.59×10^{-16}	1.07×10^{-16}	2.84×10^{-17}	3.32×10^{-18}	1.13×10^{-18}
Q (2s)	1.80×10^{-15}	4.46×10^{-16}	7.70×10^{-17}	8.14×10^{-18}	5.59×10^{-19}	2.02×10^{-19}
Q_3 (2px)	5.51×10^{-16}	4.10×10^{-16}	1.31×10^{-16}	4.63×10^{-17}	0.18×10^{-18}	4.15×10^{-19}
Q (2px)	1.05×10^{-15}	4.16×10^{-16}	1.35×10^{-16}	3.16×10^{-17}	4.41×10^{-18}	3.27×10^{-19}
Q_3 (2pz)	6.84×10^{-16}	5.65×10^{-16}	3.05×10^{-16}	9.94×10^{-17}	1.79×10^{-17}	1.61×10^{-18}
Q (2pz)	3.57×10^{-16}	2.09×10^{-16}	7.92×10^{-17}	1.87×10^{-17}	3.76×10^{-18}	5.74×10^{-19}
Q_5 (total)	2.46×10^{-15}	2.05×10^{-15}	1.54×10^{-15}	4.68×10^{-16}	7.45×10^{-17}	8.50×10^{-18}
Q (total)	4.97×10^{-15}	2.27×10^{-15}	7.40×10^{-16}	1.55×10^{-16}	2.50×10^{-17}	3.63×10^{-18}



LECTURE V

- (i) Further Remarks On Charge Transfer
 (ii) Curve - Crossing

§1. Elementary Treatments Of Some Validity At High Energies

The early work on charge transfer (H^+ on H) by Brinkmann and Kramers^(1,2) and by Oppenheimer⁽³⁾ treated the process in the first Born approximation and retained only the interaction between the incident nucleus and the active electron (or the corresponding past interaction) in the matrix element. That is they took

$$M = M_{BK} = K_{ji} \quad (5.1)$$

which equivalent to the refined fast approximation (4.15) with $S_{ij} = \delta_{ij} = 0$. The cross section, to the first order in (m/M) is then given by

$$Q_{1s,1s}^{OBK} = \frac{2^{18} Z_1^5 Z_2^5 S_i^8}{3} \left\{ S_i^2 + (Z_1 + Z_2)^2 \right\}^{-5} \left\{ S_i^2 + (Z_1 - Z_2)^2 \right\}^{-5} \quad (5.2)$$

where S_i^2 is the usual energy parameter and Z_1 and Z_2 are the nuclear charges. Similar expressions may be derived for capture into excited states⁽⁴⁾. However, when

$$Q_c = \sum_{nl} Q_{1s,nl} \quad (5.3)$$

for H^+ on H is compared with the experimental data⁽⁵⁾ taken on H_2 , (per H atom) it is found to overestimate by a factor of five at energies up to 400 kev.

Bates and Dalgarno^(4,6) and independently Jackson and Schiff⁽⁷⁾ suggested that

$$M_{\text{BDJS}} = K_{ij} + V_{\text{nn}} \quad (5.4)$$

where V_{nn} is the nuclear interaction

$$V_{\text{nn}} = - \int \phi_i^{A*} \frac{z_1 z_2}{R} \phi_j^B dr \quad (5.5)$$

was a better approximation in practice. However,⁽⁸⁾ V_{nn} vanishes in the limit $M \rightarrow \infty$. This approximation is equivalent to (4.15) ignoring distortion, neglecting $|S_{ij}|^2$ compared with unity and replacing the resulting Matrix element

$$M_{\text{BG}} = H_{ii} - K_{ij} \quad (5.6)$$

$$= K_{ij} + V_{\text{nn}} - \langle K_{ij} + V_{\text{nn}} \rangle \quad (5.6^1)$$

where $\langle \rangle$ indicates the initial static potential, by (5.4). The resulting Q_c for H^+ on H , and on He are in excellent agreement with experiment over a wide energy range⁽¹⁰⁾.

McDowell et al. are presently extending these calculations to H^+ on H^- and H^+ on L_i^+ . In these cases Coulomb forces play some role and McDowell⁽¹¹⁾ has recently shown that the correct matrix element (to the 1st order) in that case is (5.1) where the initial unperturbed eigenfunctions are now taken to be products $|U_i \rangle$ of atomic orbitals and an incoming Coulomb wave. We have

incoming Coulomb wave. We have

$$M^{CB} = \langle \psi_f | V^A(\underline{r}_1) | u_i \rangle \quad (5.7)$$

where $|u_i\rangle$ satisfies

$$[H_0 + V^A(\underline{r}_1) + V_{nn}] |u_i\rangle = E_i |u_i\rangle \quad (5.8)$$

Now the atomic functions used in Lecture (4) $|\phi_i^A\rangle$ satisfy

$$[H_0 + V^A(\underline{r}_1)] |\phi_i^A\rangle = E_i^A |\phi_i^A\rangle \quad (5.9)$$

so to the 1st order

$$|u_i\rangle = |\phi_i^A\rangle + \sum_j \frac{\langle \phi_j^A | V_{nn} | \phi_i^A \rangle}{E_i - E_j} |\phi_j^A\rangle \quad (5.10)$$

and substituting this in (5.7) we may obtain the correction due to the Coulomb potential as

$$M^{CB} = M_{Bk} + \sum_k \frac{\langle \phi_i^A | V_{nn} | \phi_k^A \rangle \langle \phi_k^A | V^A(\underline{r}_1) | \phi_j^B \rangle}{E_i - E_k} \quad (5.11)$$

That is V_{nn} scatters the incident system from state i into state k , and capture proceeds from there to the final state. The important virtual transitions are (i) the target is excited with $\Delta l = \pm 1$, and (ii) the target is unexcited but the relative momentum vector is altered. Both these contributions can be evaluated by the **Femann** technique, and calculations are in progress. The total γ^n effect is small, for $|M^{CB}|^2$ can be evaluated in closed form, and

it may be shown that if⁽¹¹⁾

$$\frac{Z_1}{k_i} \ll 1 \quad (5.12)$$

then

$$|M^{CB}|^2 \doteq |M_{BK}|^2. \quad (5.13)$$

Returning to (5.6) we may attempt to improve it by including distortion, by noting that the most important effect is the distortion of the unperturbed initial atomic eigenfunction by the incoming particle, i.e. by $V^B(\underline{r}_2)$. McDowell⁽⁸⁾ has therefore computed the cross section, replacing M_{BDJS} by

$$M_{dist} = \langle \psi_f^B | V_{nn} + V^B(\underline{r}_2) | \chi_i^A \rangle \quad (5.14)$$

where

$$|\chi_i^A\rangle = |\phi_i^A\rangle + \sum_j \frac{\langle \phi_i^A | V^B(\underline{r}_2) | \phi_j^A \rangle}{E_i - E_j} |\phi_j^A\rangle \quad (5.15)$$

which is equivalent to replacing $\langle K_{ij} + V_{nn} \rangle$ in (5.6ⁱ) by the sum in (5.15). This modification greatly decreases the cross section at low energies (<200 kev.). Calculations for He^{++} on H by this approximation are now in progress.

(ii)

Curve Crossing

If the Schrodinger equation of the quasi-molecule formed by the colliding systems is non-separable in the electron coordinates, and the potential energy curves of states ϕ_1 and ϕ_2 are known, then it is possible that $V_1(R)$ may equal $V_2(R)$ for some $R = R_x$ say. If we then proceed to a higher approximation

$$\bar{\Psi}_{1,2} = c_1^{1,2} \phi_1 + c_2^{1,2} \phi_2 \quad (5.2.1)$$

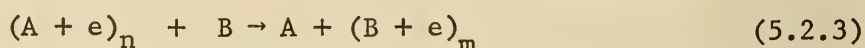
Then it is found (Moisewitsch, B. L. 1962) that the new potential energies $V_1'(R)$, $V_2'(R)$ are never equal unless ϕ_1 and ϕ_2 belong to different symmetry classes.

Landan⁽¹²⁾ and Zener⁽¹³⁾ suggested that in such cases transitions between the states corresponding to $\phi_1(R \rightarrow \infty)$ and $\phi_2(R \rightarrow \infty)$ were likely only for $R \neq R_x$. If P is the probability of such a transfer, on any one passage through R_x , then the transition probability is

$$P = 2P(1-P) \quad (5.22)$$

and is small, both when P is small and when P is large. Bates⁽¹⁴⁾ has recently criticized these assumptions, and their method of approximating P , as follows:-

Consider the transition



at some impact parameter p , under a perturbation H' .

Let

$$H_{ij} = \int \phi_i^* H' \phi_j d\tau \quad (5.2.4)$$

be a zero order matrix element, where we take ϕ_n and ϕ_m to be appropriate linear combinations of the (exact) molecular eigenfunctions and of the same symmetry class. If ψ^A describes the state in which the electron is on nucleus A as $R \rightarrow \infty$, in the zeroth order approximation, then ϕ_n is the wave function describing $\{(A + e)_n + B\}$ for $R \geq R_x$, but $\{A + (B + e)_m\}$ for $R < R_x$, and similarly for ϕ_m . Thus

$$H_{nm}(R) \neq 0 \text{ (all } R\text{)}. \quad (5.2.5)$$

Further if H is the total Hamiltonian, (since in general $A\phi_n = \sum_j A_{nj} \phi_j$ and in our case the sum runs only over $j = n, m$),

$$H\phi_n(R, \tau) = H_{nn}(R)\phi_n + H_{nm}(R)\phi_m \quad (5.2.6)$$

$$H\phi_m(R, \tau) = H_{nm}(R)\phi_n + H_{mm}(R)\phi_m$$

and at $R = R_x$

$$H_{nn}(R_x) = H_{mm}(R_x) \quad (5.2.7)$$

while

$$\Delta E_{mn}(R_x) = 2|H_{nm}(R_x)|. \quad (5.2.8)$$

We now proceed as in (4.5), taking a two state expansion

[Assumption 0]

$$\Psi_n = c_n(t)\psi_n + c_m(t)\psi_m \quad (5.2.9)$$

with

$$\psi_n = \phi_n \exp\left\{-\frac{i}{2}kz - i \int_0^t \left[H_{nn} + \frac{1}{8}m\sigma^2\right] dt'\right\} \quad (5.2.10)$$

and substitute this into

$$\left\{ H - i \frac{\partial}{\partial t} \right\} \Psi_n = 0 \quad (5.2.11)$$

A typical term yields

$$\left\{ H - i \frac{\partial}{\partial t} \right\} \Psi_n = \left[\begin{aligned} & \{ H_{nn} \Phi_n + H_{mm} \Phi_m \} \\ & + \{ H_{nn} \Phi_n - i v \frac{\partial \Phi_n}{\partial z_{r_1}} \} \end{aligned} \right] \times \quad (5.2.12)$$

$$\times \exp \left\{ -\frac{i}{2} k z - i \int^t [H_{nn} + \frac{1}{8} m v^2] dt' \right\}$$

We now make

Assumption I: Φ_n is a slowly varying function of z , $\partial \Phi_n / \partial z_{r_1} \neq 0$.

Thus

$$\left\{ H - i \frac{\partial}{\partial t} \right\} \Psi_n \doteq H_{nn} \Phi_n \exp \left\{ -\frac{i}{2} k z - i \int^t [H_{nn} + \frac{1}{8} m v^2] dt' \right\} \quad (5.2.13)$$

Using this, (5.2.11) becomes

$$\begin{aligned} & C_n H_{nn} \Phi_n \exp \left\{ -\frac{i}{2} k z - i \int^t [H_{nn} + \frac{1}{8} m v^2] dt' \right\} \\ & + C_m H_{mm} \Phi_m \exp \left\{ +\frac{i}{2} k z - i \int^t [H_{mm} + \frac{1}{8} m v^2] dt' \right\} \\ & = i \dot{C}_n \Psi_n + i \dot{C}_m \Psi_m \end{aligned} \quad (5.2.14)$$

Multiply in turn by Ψ_m^* , Ψ_n^* on the left and integrate over the electron co-ordinates, to obtain

$$i\dot{C}_m = C_n H_{mn} \exp \left\{ -i \int^t [H_{nn} - H_{mm}] dt' \right\} \\ + C_m H_{nm} \int \Phi_m^* \Phi_n e^{ikz} \underline{dr}$$

$$i\dot{C}_n = C_m H_{nm} \exp \left\{ -i \int^t [H_{mm} - H_{nn}] dt' \right\} \\ + C_n H_{mn} \int \Phi_n^* \Phi_m e^{ikz} \underline{dr}$$

(5.2.15)

and make

<u>Assumption II:</u> $e^{ikz} \doteq 1, (v \rightarrow 0).$
--

Then

$$i\dot{C}_m = C_n H_{mn} \exp \left\{ -i \int^t [H_{nn} - H_{mm}] dt' \right\}$$

$$i\dot{C}_n = C_m H_{nm} \exp \left\{ +i \int^t [H_{nn} - H_{mm}] dt' \right\}$$

(5.2.16)

It is true that near R_x

$$\frac{\partial H_{mn}}{\partial t} = 0 \quad (5.2.17)$$

and thus in this region ($t \ll 1$) a power series expansion gives, $(t = 0 \text{ at } R = R_x),$

$$(H_{mm} - H_{nn}) \doteq \alpha t \quad (5.2.18)$$

where α is a constant. We now make

Assumption III: Equation (5.2.18) is valid for all t .

We can now write (5.2.16) as

$$\begin{aligned} i\dot{C}_m &= C_n H_{mn} e^{-\frac{i}{2}\alpha t} & \} \\ i\dot{C}_n &= C_m H_{nm} e^{+\frac{i}{2}\alpha t} & \} \end{aligned} \quad (5.2.19)$$

and eliminate C_n to obtain ($f = |H_{mn}|$).

$$\ddot{C}_m + i\alpha t \dot{C}_m + f^2 C_m = 0 \quad (5.2.20)$$

This is a version of Weber's equation, and solving it by standard methods subject to the boundary conditions

$$C_n(-\infty) = 1 \quad C_m(-\infty) = 0$$

we obtain

$$|C_m(+\infty)|^2 = 1 - e^{-\omega} \quad (5.2.21)$$

with

$$\omega = 2\pi |H_{nm}|^2 \frac{\partial}{\partial t} |H_{nm} - H_{nn}|_{R_x} \quad (5.2.22)$$

yielding

$$P = e^{-\omega}. \quad (5.2.23)$$

This is the Landau - Zener result. We now examine its validity.

Taking the simplest problem first we have assumption II, that

$e^{ikz} \doteq 1$ as $v \rightarrow 0$. This will be sufficiently accurate if

$\sin(kz) < \frac{1}{2}$, or $kz < \frac{\pi}{4}$ say, so that if l is a typical linear dimension of either of the atomic orbitals involved, we will have assumption II valid if the impact energy $\epsilon_i < \epsilon_{10}$ where⁽¹⁴⁾

$$\epsilon_{10} \sim \frac{2.5 \times 10^4 M}{l^2} \text{ eV} \quad (5.2.24)$$

where M is in a.m.u. and l in atomic units. Clearly this is not a very severe restriction. Assumptions 0 and I are much more significant. They imply that both ϕ_m and ϕ_n describe S states, for if say ϕ_n is not, then $\partial\phi_n/\partial z_{\perp}$ contains appreciable components of states differing from ϕ_n in azimuthal quantum number alone.

For example, Bates (1962) points out that if ϕ_m is a p_0 state an s state transitions of the sequence $S \rightarrow p_0 \rightarrow p_{\pm 1} \rightarrow p_0 \rightarrow S$ will considerably decrease the Landau - Zener P factor. Even if the states are both s type, at sufficiently high velocity the assumption

$\partial\phi_n/\partial z_{\perp} \sim 0$ must be false. The most serious failure, however, was pointed out by Bates⁽¹⁴⁾ and this is the falsity of assumption

III. He points out that transitions are in fact likely throughout the region in which the exponential factors in (5.2.16) are

slowly varying. If the width of this zone is ΔZ , then we have,

by the method of stationary phase,

$$\frac{1}{v} \left| \int_{z_x - \frac{1}{2}\Delta Z}^{z_x} [H_{mm} - H_{nn}] dz' + \int_{z_x}^{z_x + \frac{1}{2}\Delta Z} [H_{nn} - H_{mm}] dz' \right| \sim \bar{n} \quad (5.2.25)$$

where we suppose $H_{nm}(z')$ ($z_x - \frac{1}{2}\Delta Z \leq z' \leq z_x + \frac{1}{2}\Delta Z$) is constant.

Making assumption III,

$$\frac{1}{v} \left| \int_{z_x - \frac{1}{2} \Delta z}^{z_x} \alpha z dz - \int_{z_x}^{z_x + \frac{1}{2} \Delta z} \alpha z dz \right| \sim \bar{u}$$

$$\text{or } \Delta z \sim \left(\frac{4\bar{u}v}{\alpha} \right)^{1/2} \quad (5.2.26)$$

That is, $\Delta z \rightarrow \infty$ as $v \rightarrow \infty$ and this is clearly unacceptable; so III cannot be valid. Even when v is small Δz is so large that it is not in general sufficient to treat H_{nm} as constant. When P is a maximum ($\omega = 0.69$), Bates shows that

$$\Delta z \doteq 0.5 |H_{nm}(R_x)| z_x^2$$

with H_{nm} in ev., which may be large. The correct procedure in the simple case of $s - s$ transitions, is to solve (5.2.16) as it stands to obtain ($C_m \ll C_n$)

$$P = 2 \left| \frac{1}{v} \int_{-\infty}^{+\infty} H_{nm} \exp \left\{ -\frac{i}{v} \int_0^z [H_{nn} - H_{mm}] dz' \right\} dz \right|^2 \quad (5.2.27)$$

which is very different from (5.2.23). This has not as yet been applied to any specific case.

To sum up, one concludes that the Landau - Zener formulation may be satisfactory for S-S transitions when v is well below the velocity U_m at which the maximum cross section is expected.

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LECTURE VI

Ionization Of Atomic Systems By Fast Protons

This final lecture will describe what little work has been done up to the present on the ionization of atomic systems by other atomic systems, which are usually supposed bare ions.

Following (2.13) we have for the transition

$$X^+ + Y \rightarrow X^+ + Y^+ + e \quad (6.1)$$

the electron being ejected with momentum \underline{K} ,

$$Q_{\mathcal{K}}(nl \rightarrow c) = \frac{1}{2\pi v^2} \int_{K_{\min}}^{K_{\max}} |N_{nm}|^2 K dK \quad (6.2)$$

and

$$Q_{\text{ion}}(v^2) = \int_0^{K_{\max}} Q_{\mathcal{K}}(nl \rightarrow c) d\mathcal{K} \quad (6.3)$$

where $N_{nm}(K, \mathcal{K})$ is the relevant matrix element.

Apart from some external numerical factor depending on the atomic states involved, this will in general be of the form,

$$N(nl \rightarrow c) = \int \bar{\Psi}_i(\underline{r}_j) \Xi_j^{i\mathbf{k} \cdot \underline{r}_j} \bar{\Psi}_f(\underline{r}_j) d\underline{r}_j \quad (6.4)$$

where we are now working to Born's approximation.

Now $\Psi_f(\underline{r}_j)$ is of the form,

$$\bar{\Psi}_f \sim P \left[U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{j-1}, \underline{r}_{j+1}, \dots, \underline{r}_n) \frac{\mathcal{K}}{(2\pi)^{3/2}} F(\underline{r}_j) \right] \quad (6.5)$$

where P permutes all the \underline{r}_i ($i \neq j$) with \underline{r}_j , and the j th electron is ejected, and U is the wave function of the residual ion. Here we have normalized the ejected electron wave function

$\psi_{\underline{x}}(\underline{r}_j)$ such that

$$\int \Psi_{\underline{x}}^*(\underline{r}_j) \Psi_{\underline{x}'}(\underline{r}_j) d\underline{r}_j = \delta(\underline{x}' - \underline{x}) \quad (6.6)$$

so that $F(\underline{r}_j)$ has asymptotic form

$$F(\underline{r}_j) \sim e^{i\sigma(\underline{x}) + i\underline{x} \cdot \underline{r}_j} \quad (6.7)$$

where σ is a phase factor.

Integrating over \underline{R} and all the electrons except the j th, the integral (6.4) turns out to be proportional to

$$I(nl \rightarrow c) = \int \phi(nl, \underline{r}_j) \phi(\underline{x}, \underline{r}_j) e^{i\underline{k} \cdot \underline{r}_j} d\underline{r}_j \quad (6.8)$$

Two alternative procedures are possible. If we are willing to suppose that the ejected electron moves in a Coulomb field, of some effective charge Z , we can write

$$\phi(\underline{x}, z, \underline{r}_j) = N(\underline{x}) e^{i\underline{n} \cdot \underline{z} / \underline{x}} e^{i\underline{x} \cdot \underline{r}_j} F\left[-\frac{i\underline{z}}{\underline{x}}, 1, i\underline{x} \cdot \underline{r}_j - i\underline{x} \cdot \underline{z}\right] \quad (6.9)$$

and perform the integration by standard methods, provided

$\phi(nl, \underline{r}_j)$ has a reasonably simple analytic form. For hydrogen ($z = 1$) this is of course exact, and the calculations for both H^0 and H^+ impact have been performed by Bates and Griffing^(1,2) and are shown in Fig. (6.1).

The alternative procedure is to expand $\phi(\underline{x}, \underline{r}_j)$ in partial waves,

$$\phi(\underline{x}, \underline{r}_j) = \sum_{\ell} (2\ell + 1) i^{\ell} e^{i\sigma_{\ell}} R_{\underline{x}\ell}(r) P_{\ell}(\cos\theta) \quad (6.10)$$

where $R_{\kappa \ell}(r)$ is the solution of the Schrödinger equation for an electron in the field of Y^+ ($n'l'$), having an electron of momentum κ in the ℓ' wave of the continuum. The cross section then becomes

$$Q_{ion} = \frac{\text{const}}{S_i^2} \sum_{\ell'} (2\ell'+1) Q_{\ell'}(S_i) \quad (6.11)$$

with

$$Q_{\ell'}(S_i) = \int_0^{\kappa_{max}} G_{\kappa, \ell'}(S_i) \kappa d\kappa \quad (6.12)$$

$$G_{\kappa, \ell'}(S_i) = \int_{\kappa_{min}}^{\kappa_{max}} |G_{\kappa, \ell'}(K)|^2 K^{-3} dK \quad (6.13)$$

$$G_{\kappa, \ell'}(K) = \int P(n\ell, r) P(\kappa \ell', r) j_{\ell}(Kr) dr \quad (6.14)$$

Here $P(n\ell, r) = r R(n\ell, r)$, and j_{ℓ} is the usual ℓ th order spherical Bessel function.

§2. We now discuss the application of these procedures to atoms other than hydrogen.

(i) Helium. This has been investigated by Erskine⁽³⁾, Dalgarno and McDowell⁽⁴⁾, Mapleton⁽⁵⁾, and Grosjean and V. d Waale⁽⁶⁾. All the above authors represent the ground $1s$ state by a simple one parameter variational wave function

$$\phi(1s, r) = \frac{z_1^{3/2}}{\sqrt{\pi}} e^{-z_1 r} \quad ; \quad z_1 = 1.69 \quad (6.15)$$

Mapleton takes

$$\phi(\kappa l', r) = N(\kappa) e^{i\kappa r} F \left[\frac{iZ_2}{\kappa}, 1, i\kappa r - i\kappa \cdot r \right] \quad (6.16)$$

With this choice one must take $Z_2 = Z_1$ to ensure orthogonality, otherwise one obtains a cross section tending to a finite limit as $E_1 \rightarrow \infty$. (Fig. 6.1). However, asymptotically one has a Coulomb field with $Z_2 = 1.0$. A better choice therefore is to expand (6.16) in partial waves and take

$$\begin{aligned} Z_2 &= Z_1 & \ell &= 0 \\ Z_2 &= 1 & (\ell \neq 0) \end{aligned} \quad (6.17)$$

His results for this case are in excellent agreement with experiment^(7,8) (Fig. 6.2) and with the calculations of Erskine, who ignored the $\ell = 0$ contribution and took $P(\kappa, \ell = 1, r)$ to be the solution of the Hartree equation

$$\frac{d^2 P(\kappa \ell, r)}{dr^2} + \left\{ \kappa^2 + \frac{Z}{r} \left[1 + (1+2r) e^{-4r} \right] - \frac{\ell(\ell+1)}{r^2} \right\} P(\kappa \ell, r) = 0 \quad (6.18)$$

as did Grosjean and V. d Waale. Dalgarno and McDowell solved (6.18) with a numerical potential term, and used this to obtain $Z_2(\kappa)$ for the p - wave, evaluating the other contributions with the same $Z_2(\kappa)$.

(ii) Lithium. McDowell and Peach⁽¹³⁾ pointed out that in this case there is no choice of Z_2 which will ensure orthogonality, and that the cross section with Coulomb waves diverges for all Z_2 . However, the dominant p - wave contribution is finite and was

computed for $Z_2 = Z_1$ and $Z_2 = 1$, (Fig. 6.3), and is clearly very sensitive to the choice of Z_2 . They show that the corresponding photoionization cross section varies as $Z_2^7 \exp\{-\beta Z_2\}$. Even for $Z_2 = 1$, Q_{photo} is sensitive to the choice of bound state wave function. (Table 6.1)

TABLE 6.1

Photoionization cross sections of Li (10^{-18} cm^2) with Coulomb function $Z=1$ and (a) 3 - parameter bound function (Holoien 1958)⁽⁹⁾
 (b) 9 - parameter bound function (Roothan et al., 1960)⁽¹⁰⁾

κ^2 (Rydbergs)	a	b	c
0	0.769	0.513	2.50
0.01	0.819	0.547	---
0.02	0.869	0.634	2.40
0.03	0.915	0.726	---
0.04	0.956	0.779	2.20
0.05	0.982	0.772	---

"c" indicates the experimental results of Tunstead (1953).⁽¹¹⁾

This implies that the agreement between Mapleton's calculations and the experimental results may well be fortuitous.

McDowell and Peach are now recomputing Q_{ion} for H^+ on Li using Hartree - Fock wave functions for the ejected electron and a 3-parameter Holoien function for the bound state.

(iii) Other Calculations.

Bates and Griffing^(1,2), McDowell and Peach^(12,13), and Bates, McDowell and Omholt⁽¹⁴⁾ have calculated the energy distribution of the ejected electrons at energy E_1 , from H, H^- , Li and Ne respectively for either H^+ or H^0 impact. They find it depends primarily on the initial angular momentum l , as would be expected from consideration of the photoionization cross sections. Rudd has extended this work to He using Mapleton's calculations, and finds reasonable agreement with experiment.⁽⁸⁾ (Fig. 6.4).

(iv) Classical Calculations.

Rudd (loc. cit.) and Alsmiller⁽¹⁵⁾ have applied Grsinskis' modification of Thompson's method to calculate Q_{ion} for H^+ on He and H_2 respectively. (Fig. 6.2 and 6.4). They obtain surprisingly good agreement with the observations, considering the nature of the approximation. [In this method one assumes that if the ion passes at impact parameter p it will transfer energy $\Delta E(p, v)$ to an electron of velocity v , and computes the cross section as

$$Q_2 = -2\bar{u} \int \frac{1}{2\bar{u}\bar{v}^2} \delta(v - \bar{v}) \int_{p(v)}^0 p dp dv \quad (6.19)$$

where \bar{v} is the expectation value of the velocity and $p(v)$ is the greatest impact parameter for which $\Delta E(p, v)$ exceeds the ionization potential.]

FIG. 6.1. IONISATION OF HELIUM BY FAST PROTONS. $\log_{10} Q$ CROSS SECTION IN $\bar{u}a_0^2$ AGAINST $\log_{10} E_p$ (IMPACT ENERGY E_p IN KEV)

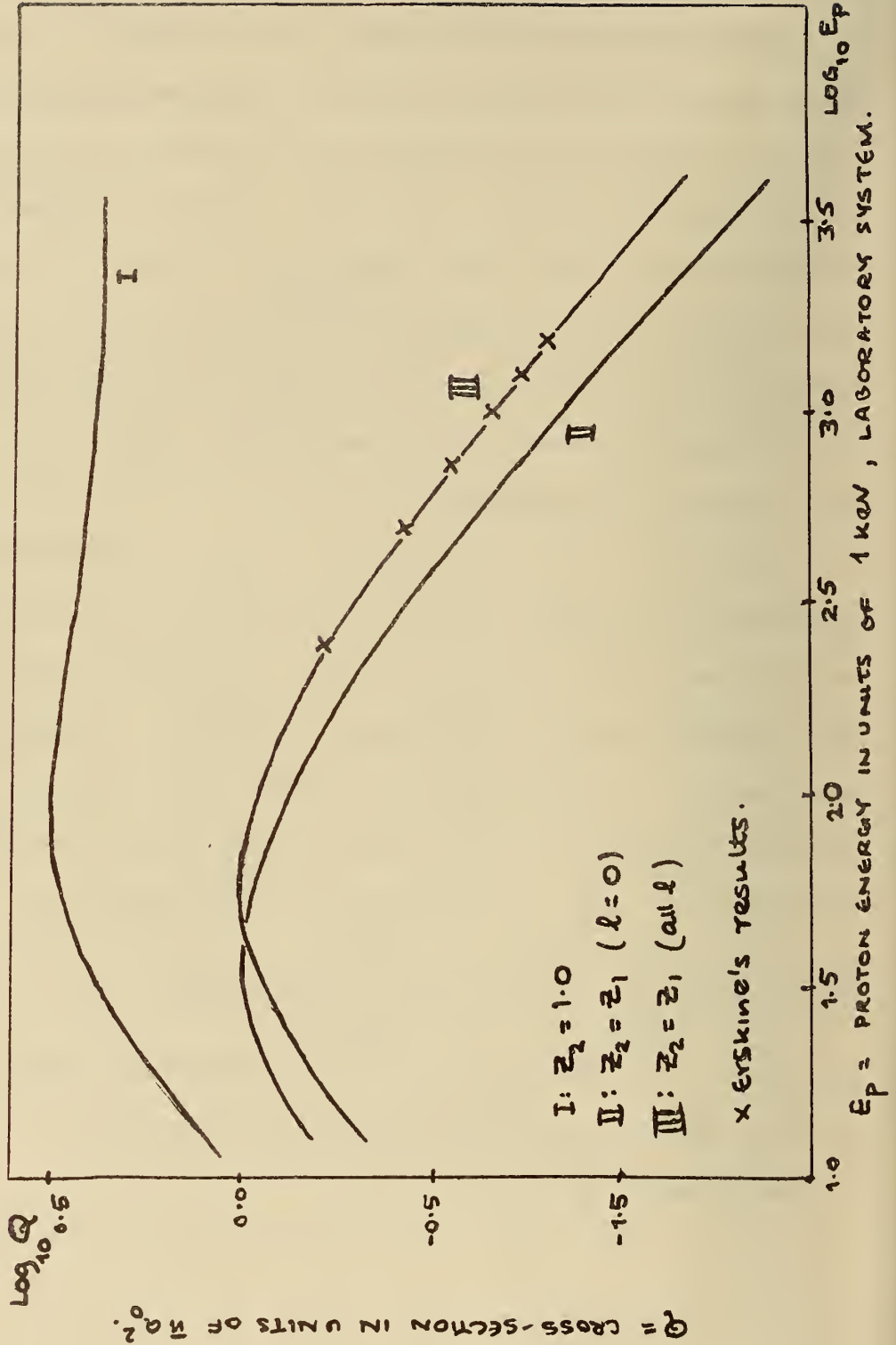


FIG. 6.2. IONISATION OF HE BY H^+ , (RUDD & JORGENSEN, 1962)

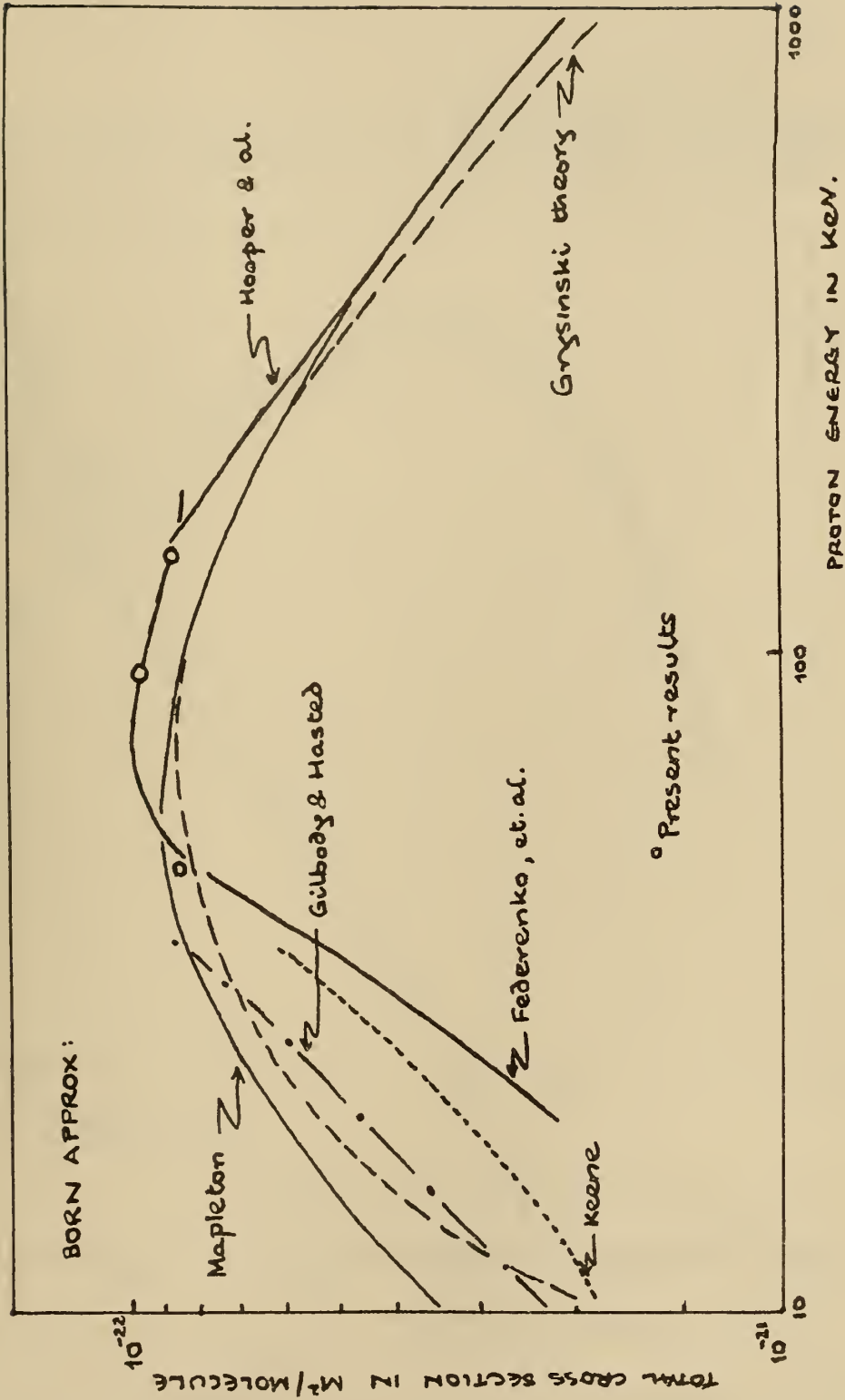
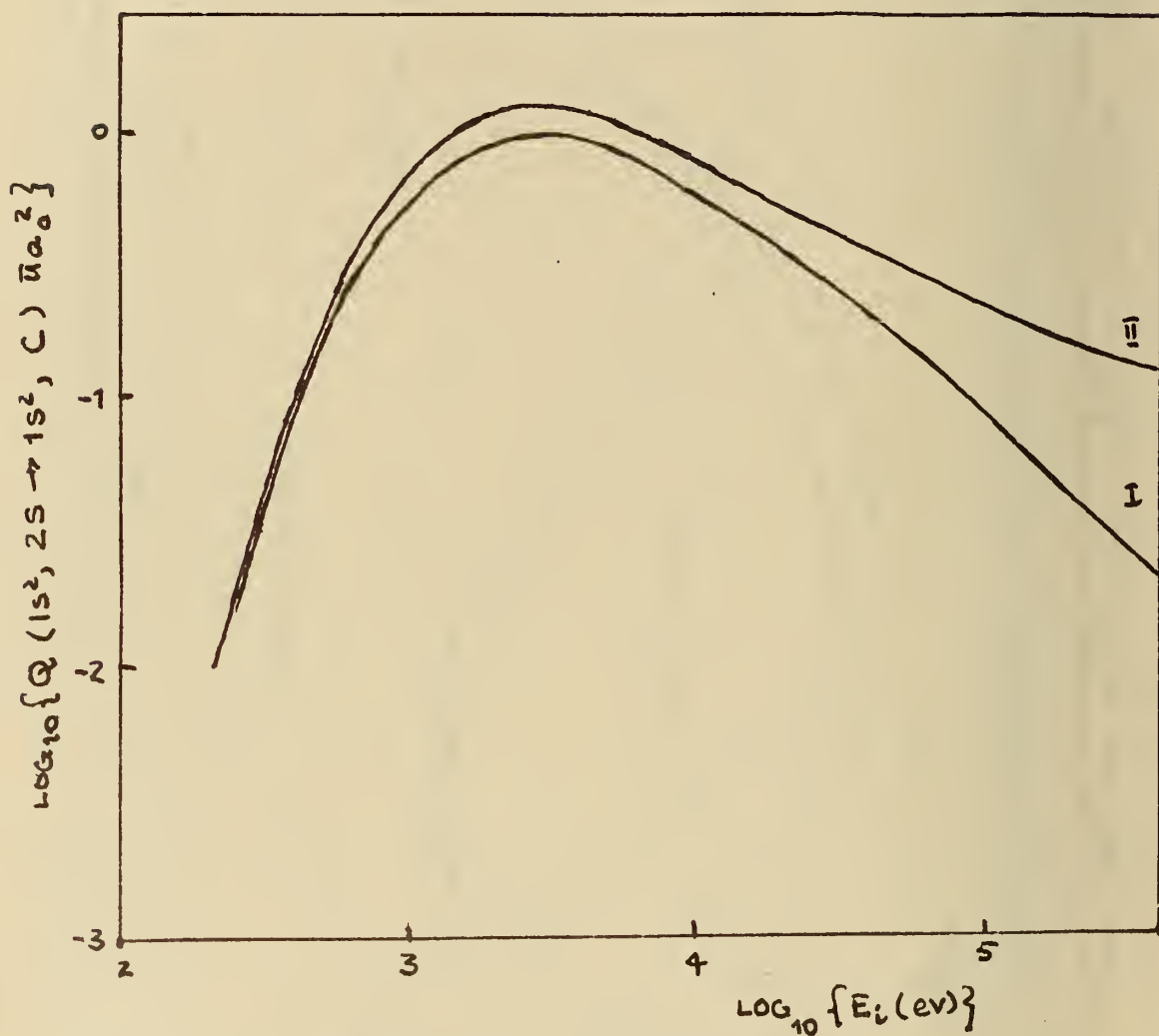


FIG. 6.3. IONISATION OF LITHIUM BY PROTON IMPACT.



I: p-wave Born $Z_1 = Z_2 = 2.67$.

II: Total cross-section $Z_1 = Z_2$

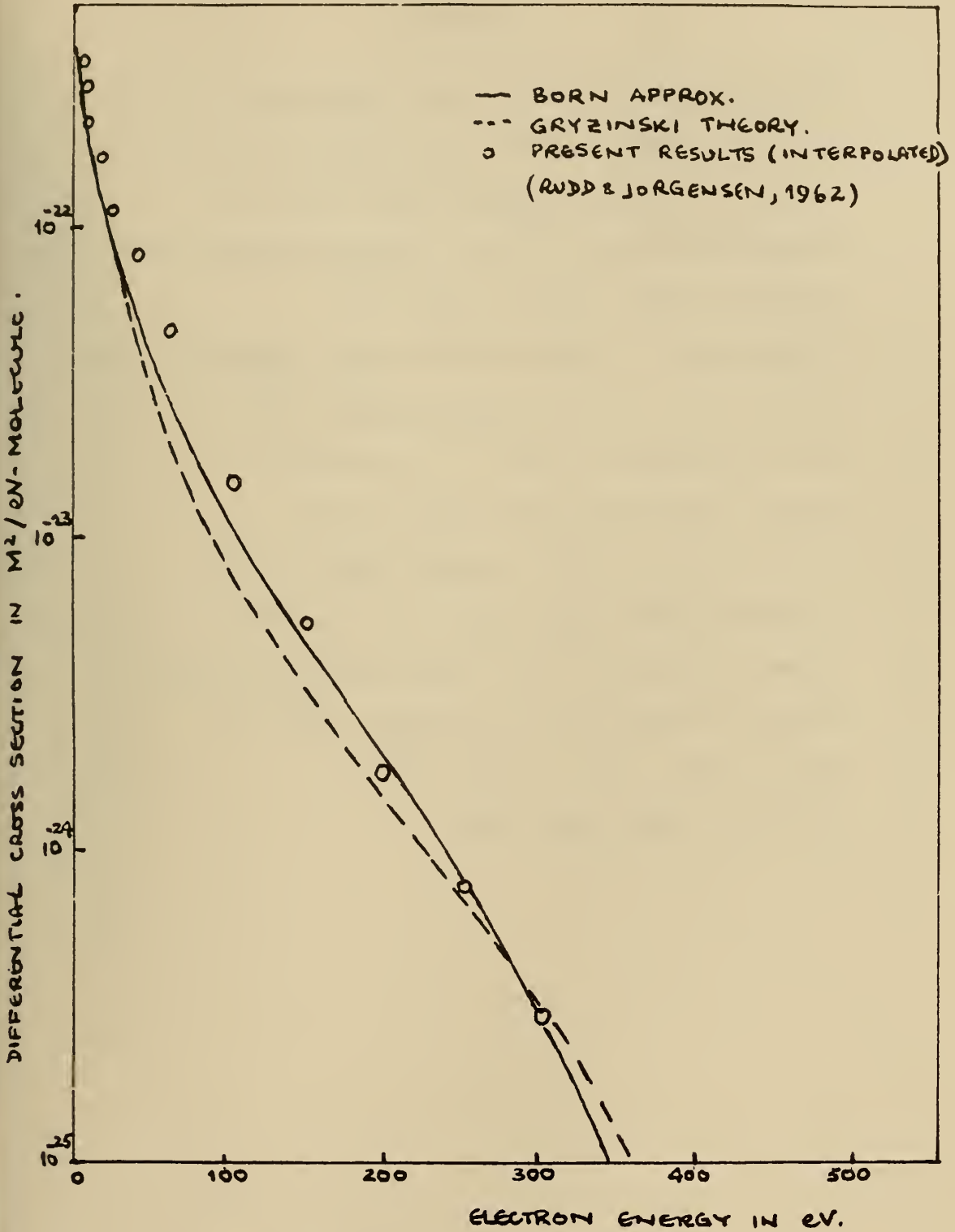
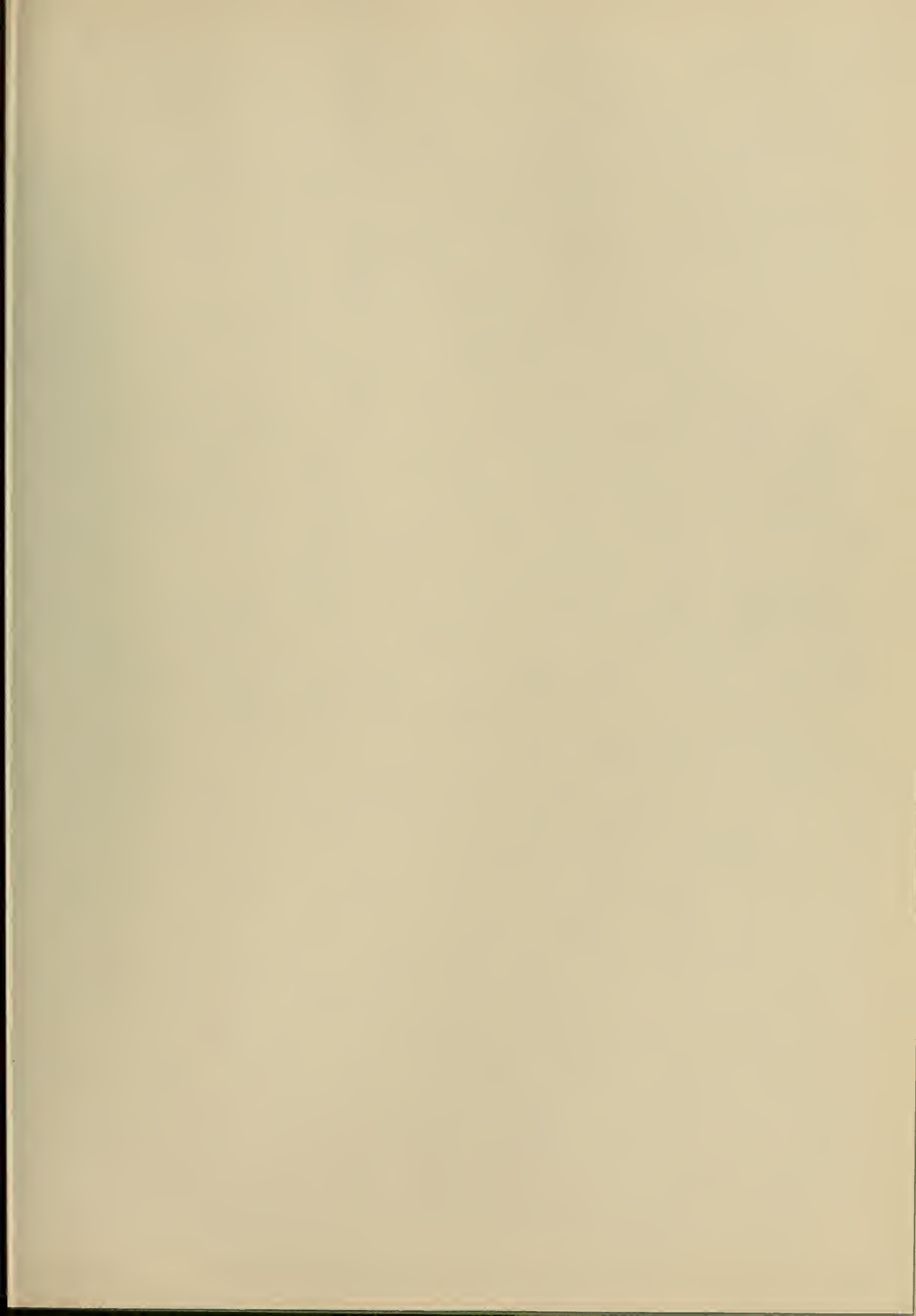


FIG. 6.4. IONISATION OF He BY H^+ ; ELECTRON DIST.^N

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