REVIEWS OF MODERN PHYSICS VOLUME 34, NUMBER 3 JULY, 1962

The Low-Energy Scattering of Electrons and Positrons by Hydrogen Atoms*

P. G. BURKE
Lawrence Radiation Laboratory, Berkeley, California

AND

KENNETH SMITH
Argonne National Laboratory, Argonne, Illinois

CONTENTS

I. INTRODUCTION

THIS review is concerned with the elastic and inelastic (excitation, pickup, or ionization) collisions of slow electrons or positrons with hydrogen atoms. The purpose of this paper is to present a survey of the experiments that have been reported to date and to review the many theoretical attempts to calculate the relevant cross sections within the framework of nonrelativistic wave mechanics.

Most of the theoretical techniques discussed here may be generalized to more complex physical systems. For example, the collisions of electrons with gas molecules, collisions between atoms, the collisions of mesons with molecules, etc. For detailed discussions of these processes the reader is referred elsewhere.[1,2]

We follow Massey[2,3] in the definition of a "slow" collision. A collision is said to be "slow" when the relative velocity of the incident particle and target hydrogen atom is not great compared with the velocity of the atomic electron. When this criterion is not satisfied, the collision is said to be fast and the first Born approximation[4] provides a satisfactory theoretical description of the collision process.

The importance of the collision problems considered here is twofold. First, they are the simplest collision problems that can be treated by wave mechanics (nucleon-nucleon scattering involves fewer particles, but the interaction is unknown); even then, mathematical approximations must be developed to solve these problems. Currently, experimental information is becoming available on the electron-hydrogen atom problems and so it is becoming possible to evaluate the merits of the various theoretical approximations in those problems for which

---

* Work performed under the Auspices of the U. S. Atomic Energy Commission.

[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1949), 2nd ed.

[2] H. S. W. Massey, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 36.

[3] H. S. W. Massey, Revs. Modern Phys. **28**, 199 (1956).

[4] W. Kohn, Revs. Modern Phys. **26**, 292 (1954).

no mathematical estimate of the error incurred in the approximations exists. As soon as the range of validity of these approximate methods is established, they can be used with somewhat greater confidence in other problems of physical interest. Secondly, the scattering of electrons by hydrogen atoms has applications in astrophysics,[5] and the results of such investigations probably bear directly on the understanding of controlled thermonuclear devices.

In connection with the development of approximate methods for the treatment of collision problems, we are justified in examining, theoretically, the scattering of slow positrons by atoms. Furthermore, the recent developments of experimental technique associated with the study of positronium formation focusses additional interest on the fate of a stream of positrons in a gas.

In Sec. II we summarize the current experimental situation, which is completely dominated by the work of Fite and his collaborators. Four experiments have been performed on the elastic scattering of electrons by hydrogen atoms, at energies below the threshold for excitation. There is reasonable agreement among the results of three of these experiments. Two experiments have been performed on the relative cross section for the production of metastable $H(2S)$. The two sets of results differ quite substantially in magnitude, probably due to the different normalization procedures. This discrepancy is considered in detail in Sec. VII. One experiment has been carried out to measure the relative total cross section for the observation of Lyman-α radiation. The ionization cross section has been measured in four experiments, two of which were normalized to the Born approximation whereas the remaining two were absolute determinations. The results of the latter differ by 25% at 100 eV, the lowest energy where comparison is possible.

In low-energy positron or electron scattering from atomic hydrogen, it is to be expected that the atomic charge cloud will be appreciably distorted due to the impinging particle spending a great deal of time in its vicinity. The basic theoretical problem is to make adequate allowance for this distortion. In Sec. III we develop the eigenfunction expansion approach to this problem, basing the formulation on a variational principle. Qualitatively, for bombarding energies below the first excitation threshold ($k^2 < 0.75$) distortive effects are allowed for by assuming virtual transitions to the higher atomic states. The results of calculations performed in this approach are given in Sec. IV. Since the technique of expanding in terms of orthonormal functions is the method most often used in wave mechanical collision problems, one of the major tasks of this review is to investigate the rate of convergence of such expansions.

In Sec. V we summarize the principal results of recent work in developing rigorous minimum, or maximum, principles rather than the stationary principles of Sec. III. These important results, besides giving more practical meaning to variational computations, elucidate the relative importance of the various physical effects contributing to the distortion. The importance of these extrema principles cannot be stressed enough since they provide the first mathematical estimate of the error incurred in wave mechanical scattering calculations. Therefore, it is possible to make statements about the "goodness" of a theoretical result *without* appealing to experiment. This has particular significance in the present class of problems, where the experimental results reported to date make liberal use of various theoretical estimates both for normalization purposes, and for allowance of background processes.

In Sec. VI we survey other theoretical methods currently in use in electron or positron-hydrogen atom collisions, some of these still based on a variational principle. These methods, with the exception of the impulse approximation and the Born approximation, have been used only in calculations for incident energies below the first excitation threshold.

Atomic units are used throughout this article, that is, energies (labeled k^2 for the projectile) are quoted in Rydbergs, cross sections in units of πa_0^2, and phase shifts in radians.

II. EXPERIMENTS

Although calculations on the scattering of slow electrons by hydrogen atoms have been performed continuously since the early 1930's,[1] there has been very little experimental data[6] to compare with the theoretical predictions until recently. The principal reason for the lack of data is due to the difficulties encountered in performing scattering experiments for those elements that are not monatomic at room temperature. For such elements, the molecule must first be dissociated; the dissociation process is accompanied by the formation of excited states of the atom, free electrons, and ions, which in turn give rise to effects that are difficult to allow for.

The key to the solution of the experimental diffi-

---

[5] T. L. John, Monthly Notices Roy. Astron. Soc. (London) **121**, 41 (1960).

[6] H. Maecker, T. Peters and H. Schenk, Z. Physik **140**, 119 (1955); A. A. Kruithof and L. S. Ornstein, Physica **2**, 611 (1935).

culties was found in the use of modulated beam techniques. These methods were developed for the e^-H problem independently and simultaneously (1954–55) by Bederson and his co-workers at New York University, and by Boyd, Fite, and Green at University College, London.

The recent developments of experimental technique[7] associated with the study of the collision processes of a stream of positrons in a gas justifies as detailed a theoretical analysis as possible of the various reactions involved. Unfortunately, no experiments have been carried out, as yet, on the collision of positrons and hydrogen atoms.

(a) Elastic Scattering

Bederson *et al.*[8] have used an atomic beam apparatus to measure the total elastic scattering cross section for the scattering of low energy (below 14.5 eV) electrons by hydrogen atoms. In this experiment, the molecules of hydrogen were dissociated by a microwave discharge, and the beam was modulated by a mechanical chopper. Charged particles were removed from this beam (mixture of H and H_2) by electrostatic deflection, while the ratio of atomic to molecular content in the beam was determined by a Stern-Gerlach experiment. An electron beam was produced by an electrostatically focused electron gun and crossed the atomic beam at right angles. The scattered electrons gave rise to a signal, which occurred at the beam modulation frequency, and were collected by a Faraday cage. Absolute values for the atomic cross sections were obtained by normalizing to the molecular cross sections, which were in turn normalized to a curve of Normand.[9] Bederson's results are reproduced in Fig. 1.

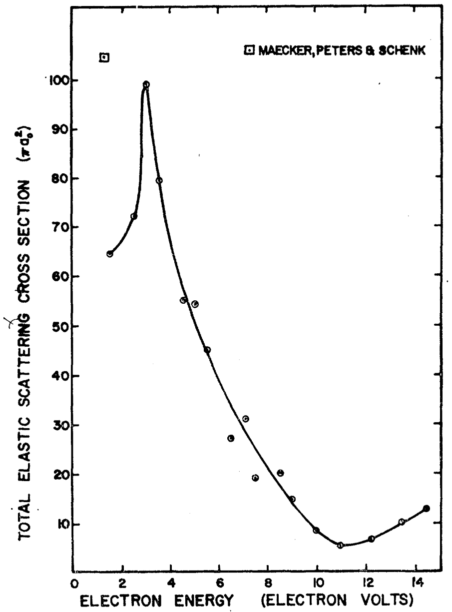


FIG. 1. Total experimental cross section vs energy for e^-H, reference 8.

The results of Bederson's measurements disagree with all calculations that have been performed to date. This disagreement between the theoretical predictions and experiment led Brackmann *et al.*[10] to remeasure the total elastic scattering cross section, using a modulated atomic beam, produced by thermal dissociation in a tungsten furnace. In this experiment, the only electrons detected were those which were scattered into a cone of $\pi/4$ half-apex angle whose axis lay in the equatorial plane of the scattering sphere. In this way about 10% of the total number of scattered electrons were collected.

In the General Atomic experiments, the relative proportions of atoms and molecules in the mechanically chopped atomic beam are determined by a mass spectrometer. In this way, measurements were made of the ratio of cross sections of the hydrogen atom and the molecule for scattering *into the observation cone.* The molecular cross section was obtained by integrating the differential cross section measured by Ramsauer and Kollath.[11] Hence, the elastic atomic cross section can be determined as absolutely as were the measurements on the molecule. The results of Brackmann *et al.*[10] are reproduced in Fig. 2; the authors attribute the large scatter of points to be due to uncertainties in the energy of the electrons.

In order to relate the results of Fig. 2, which are only for those electrons scattered into the cone of observation, to the total scattering cross sections, Brackmann *et al.*[10] devised the approximate formula

$$Q_{\text{total}} = 6.85\, Q_{\text{cone}} + 0.6\, Q_1\,, \qquad \text{(II.1)}$$

where Q_1 is the $l = 1$ partial-wave cross section (see Sec. III). Thus, the total cross section inferred from this experiment depends on assumptions concerning the angular distribution: For an isotropic distribution $Q_1 = 0$; for the various theoretical values for Q_1 [see Sec. VII (b)], Q_{total} varies; if d waves and higher

---

[7] M. Deutsch, Progr. in Nuclear Phys. **3**, 131 (1953); W. B. Teutsch and V. W. Hughes, Phys. Rev. **103**, 1266 (1956); S. Marder, V. W. Hughes, C. S. Wu, and W. Bennett, *ibid.* **103**, 1258 (1956); F. F. Heymann, P. E. Osmon, J. J. Veit, and W. F. Williams, Proc. Phys. Soc. (London) **78**, 1038 (1961).

[8] B. Bederson, H. Malamud, and J. Hammer, Bull. Am. Phys. Soc., **2**, 172 (1957); College of Engineering, Research Div., NYU, Tech. Rept. No. 2, Electron Scattering Project, Contract No. ONR-285(15) (1958) (unpublished).

[9] C. E. Normand, Phys. Rev. **35**, 1217 (1930).

[10] R. T. Brackman, W. L. Fite, and R. H. Neynaber, Phys. Rev. **112**, 1157 (1958).

[11] C. Ramsauer and R. Kollath, Ann. Physik **12**, 529 (1932).

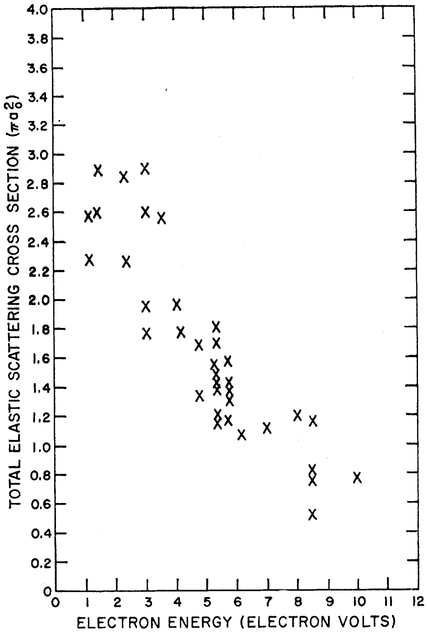


FIG. 2. Total experimental cross section vs energy for the scattering of electrons into the experimental cone of observation.[10]

partial waves contributed, then the above formula would be inadequate. However, if this formula is used, together with any of the calculated values for Q_1, the resulting total cross sections are considerably smaller than those of Bederson *et al.*[8]

One reason for the disagreement between these two experiments was thought to be the possibility of strong forward scattering, which would be missed in the General Atomic experiment. In order to test this, the General Atomic group of Gilbody *et al.*[12] measured the angular distribution of electrons elastically scattered by atomic hydrogen in the energy range from 3.8 to 10 eV for angles from 30 to 120°. Their results are reproduced in Fig. 3,[12a,b] and again were normalized to the molecular data of Ramsauer and Kollath. In this experiment, the scattering at different angles was effected by rotating the electron gun rather than the detector system. Their results (where the error in determining the absolute value of the cross section may be ±20%) indicate that the angular distribution tends to become horizontal over the observed angular range with decreasing energy, giving support to the results of reference 10.

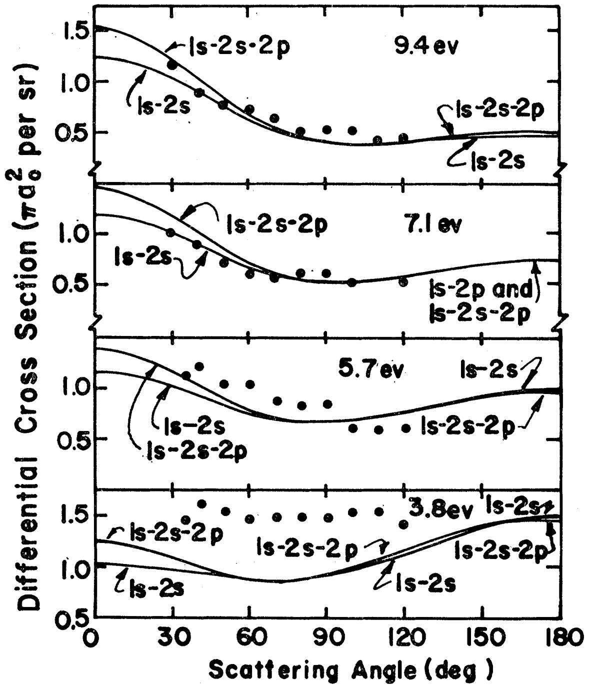


FIG. 3. e^-H differential cross section[12] at various energies compared with calculations of 1s-2s[12a] and 1s-2s-2p[12b] approximations.

Neynaber *et al.*[13] have remeasured this cross section with an experimental arrangement (again of the modulated atomic beam type) designed to collect most of the scattered electrons (actually their angular resolution was about 25°). The atomic cross sections were calculated again from the atomic to molecular ratio, whereas the molecular cross sections were taken as the arithmetic average of Normand[9] and Brüche.[14] The total cross sections measured in this experiment are given in Fig. 4, and support the lower values of references 10 and 12, rather than Bederson's results.

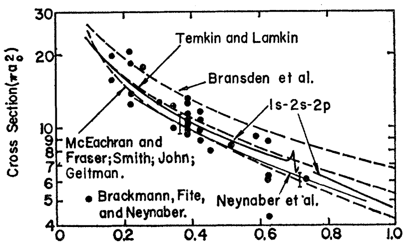


Fig. 4. Total measured collision cross sections for electrons scattered by atomic hydrogen[13] compared with several theoretical calculations.

A comparison of the above experimental results with theory is given in Sec. VII (b).

---

[12] H. B. Gilbody, R. F. Stebbings, and W. L. Fite, Phys. Rev. 121, 794 (1961).

[12a] K. Smith, R. P. McEachran, and P. A. Fraser, Phys. Rev. 125, 553 (1962).

[12b] P. G. Burke, and H. M. Schey, Phys. Rev. 126, 147 (1962); McEachran and Fraser are extending this work using the numerical method described in reference 57.

[13] R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. 124, 135 (1961).

[14] E. Brüche, Ann. Physik 82, 912 (1927).

(b) Inelastic Scattering

Fite and his collaborators[15,16] have performed an experiment to measure the cross section for excitation of Lyman-alpha radiation on electron impact. This radiation corresponds to a transition from the $n = 2$ to the $n = 1$ state. In this experiment, a highly dissociated ($> 90\%$) modulated hydrogen beam was crossed by an electron beam. The region of interaction of the two beams was viewed by a Lyman-alpha photon counter. Since the beam is not wholly dissociated, then the signal at the photon counter arises from both molecules and atoms; therefore, it is necessary to determine the ratio of atomic to molecular cross sections for excitation of the countable ultraviolet radiation (Lyman-α).

Since Lyman-α radiation is electric dipole radiation, the cross section per unit solid angle for photon emission $q(\theta)$, is related to the total cross section Q by

$$q(\theta) = 3Q(1 - P\cos^2\theta)/(3-P)\,, \qquad \text{(II.2)}$$

where θ is the angle between the direction of photon emission and the direction of the incident electron beam and $P(k^2)$ is the polarization fraction.[17] The signal strengths are proportional to $q(\theta)$ and, therefore, to the total cross section, at $\cos^2\theta = 1/3$. Relative total cross sections were measured by observing photons emitted at 54.5° ($\cos^2\theta = 1/3$) from the direction of the electron beam. These measurements agreed, to within experimental error, with relative measurements for the total cross section made at 90 and 45°. The problem of calculating P is discussed in Sec. III (b).

Whereas several processes[15] might lead to the emission of the observed Lyman-α radiation, it is probable that the major contribution at energies greater than 100 eV, comes from $1S$-$2P$ excitation. Those atoms which are excited to the $2P$ state, lifetime of the order of 10^{-9} sec., decay with emission of Lyman-α radiation while still in the collision region. Furthermore, since an ionization experiment (see below) had given confidence in the Born approximation, Fite *et al.*[15,16] normalized their curve of the relative total cross section to that of the Born approximation values for the excitation cross section $Q(1S$-$2P)$ over the energy range 200–700 eV. Their results are reproduced in Fig. 5. The Born approximation values for this cross section are compared with other approximations in Sec. VII.

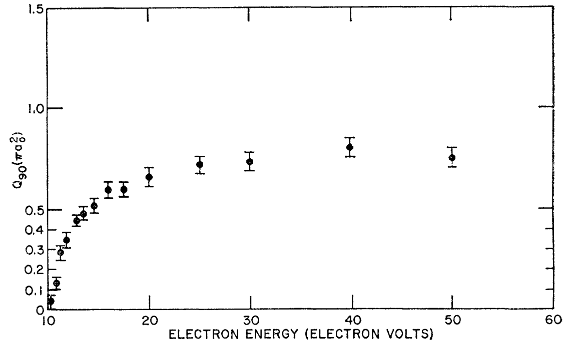


FIG. 5. Experimental cross section vs energy for the excitation of Lyman-α radiation by electron impact.[15,16]

The excitation function for the metastable $2S$ state of atomic hydrogen, $Q(2S)$, by electron impact has been measured from threshold (0.75 ry) to 45 eV by Lichten and Schultz.[18] At incident electron energies below (8/9 ry) 12.1 eV, the metastable $H(2S)$ atoms (with a lifetime of several msec) are produced only by excitation of the $2S$ state. At higher electron bombarding energies, the population of the $2S$ state also results from cascade from higher atomic states, which have been excited in the collision region.

In this experiment, an electric field was applied between the detector (an untreated platinum surface) and the electron gun in order to quench the $H(2S)$ atoms. The Lyman-α photons so produced caused electron ejection at the platinum surface, which was measured by a conventional electrometer circuit. Lichten and Schultz normalized their results in two independent ways. First, at 11.7 eV, they used a value of the yield of the detector to obtain a maximum total cross section $\sigma_T(2S) = (0.28 \pm 0.14)\pi a_0^2$. Secondly, by subtracting the contribution of the cascade processes from $Q(2S)$, they normalized their subtracted results to the Born approximation for $Q(1S$-$2S)$ at 45 eV. A discussion of their subtraction procedure as well as the validity of the Born approximation as 45 eV is given in Sec. VII. Their subtraction procedure uses the following approximate formula for the cross section for production of metastable H by all atomic processes:

$$\sigma_P(2S) = \sigma_T(2S) + 0.21\sigma(3P)\,, \qquad \text{(II.3)}$$

where σ_T is replaced by σ_{Born} at the normalization energy and $\sigma(3P)$ is an estimated cross section for $Q(1S$-$3P)$ obtained by normalizing the $Q(1S$-$2P)$ results of Fite and Brackmann[15] to the Born values for $Q(1S$-$3P)$.[19] The Born normalized results for $Q(1S$-$2S)$ are shown in Fig. 6.

---

[15] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1151 (1958).

[16] W. L. Fite, R. F. Stebbings, and R. T. Brackmann, Phys. Rev. **116**, 356 (1959).

[17] J. A. Smit, Physica **2**, 104 (1935).

[18] W. Lichten and S. Schultz, Phys. Rev. **116**, 1132 (1959).

[19] See reference 2, p. 354.

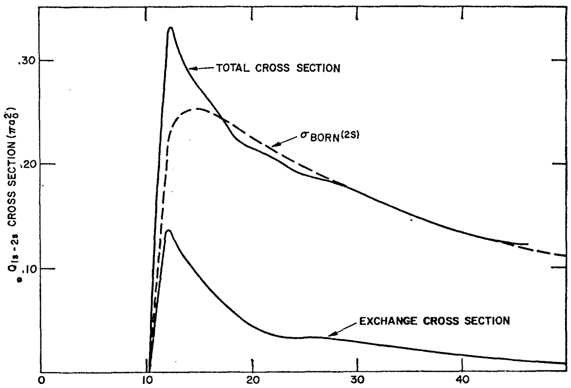


FIG. 6. Experimental cross section vs energy for 1s − 2s excitation for e^{-}H collisions.[18]

The General Atomic group, see Stebbings *et al.*,[20] have used their modulated atomic beam apparatus to measure the excitation function for metastable H(2S). In this experiment an iodine-vapor-filled Lyman-α photon counter was mounted on a movable trolley so that it could be positioned to view either the region of interaction (photon intensity due to excited 2P atoms) of the crossed beams or the "quench" region (where an electrostatic field quenched the metastable H). The lifetimes of the two states allow this separation to take place. By comparing the intensity of the photons emitted from the interaction region with the intensity from the quench region it was possible to measure the excitation function for the metastable H(2S) state relative to that of $Q(2P)$. Using the Born normalized values for $Q(2P)$,[16] Stebbings *et al.* obtained the cross sections for production of 2S metastable atoms as plotted in Fig. 7 (including the correction factor of 3/2 pointed out by Lichten[21]). These results are seen to be considerably below those reported by Lichten and Schultz, although the structures of the two curves are very similar. Thus, the question of normalization appears to be of crucial importance (see Sec. VII). In Fig. 8 we give the measured[20] angular distribution of 2S atoms, as a function of electron energy, at fixed angles.

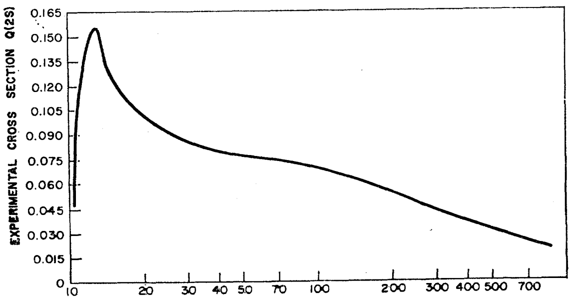


FIG. 7. Experimental cross section for the production of $H(2s)$ on electron impact.[20,21]

(c) Ionization

Fite and Brackmann[22] have used the modulated crossed beam techniques, described briefly in earlier paragraphs, in order to measure the cross section of ionization of the hydrogen atom on electron impact as a function of electron energy. The positive ions, formed by ionization of the atomic beam, are taken into a mass spectrometer, where the alternating current, at the beam modulation frequency, is used to study the ionization process. Two types of observations were made.

In the first experiment, the ratio of the cross sections for ionization of the atom and the molecule was determined. The absolute atomic cross sections were determined by multiplying this ratio by the known molecular ionization cross sections, as measured by Tate and Smith.[23] In the second experiment, Fite and Brackmann made use of the fact that the number of ions produced per second, when an electron beam crosses a gas of fixed number density of neutral particles, is proportional to $\sigma(E)$ and I. Here $\sigma(E)$ is the cross section for ionization at the particular electron bombarding energy E, and I is the electron current. Hence, the ratio of the cross sections at two electron energies, $\sigma(E_1)/\sigma(E_2)$ is given by the ratio of the positive ion-signal strengths divided by the respective electron currents at the two energies. These relative cross-section curves were normalized to the values calculated in the Born approximation at 500 eV. The results from both sets of data are presented

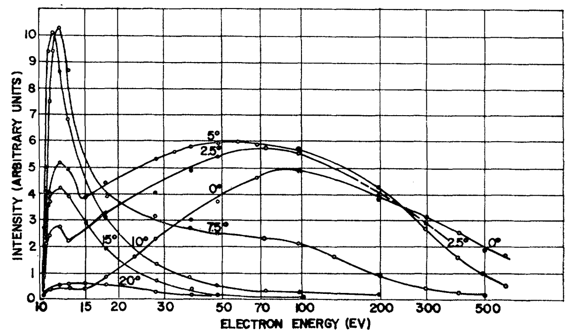


FIG. 8. Angular distribution of H(2s), showing dependence on electron energy at fixed angles.[20]

---

[20] R. F. Stebbings, W. L. Fite, D. G. Hummer, and R. T. Brackmann, Phys. Rev. **119**, 1939 (1960).

[21] W. Lichten, Phys. Rev. Letters **6**, 12 (1961).

[22] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).

[23] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

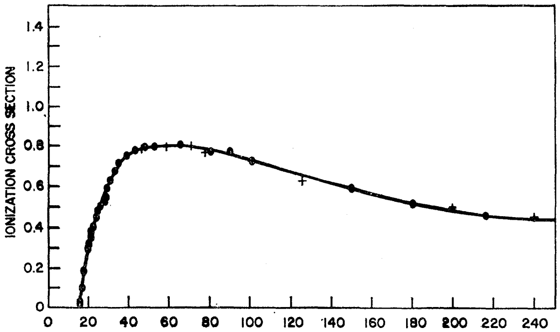


FIG. 9. Experimental cross section for ionization of atomic hydrogen by electrons.[22] Dots are relative cross sections normalized to the Born approximation at 500 eV. Crosses are measurements relative to the molecular-ionization cross section.

in Fig. 9. It was found that there was complete agreement between the absolute determinations of the ionization cross section and the Born approximation for energies greater than 200 eV. This fact demonstrates the validity of the Born approximation in the high-energy region and was the evidence used to justify the normalization of $Q(1S\text{-}2P)$.

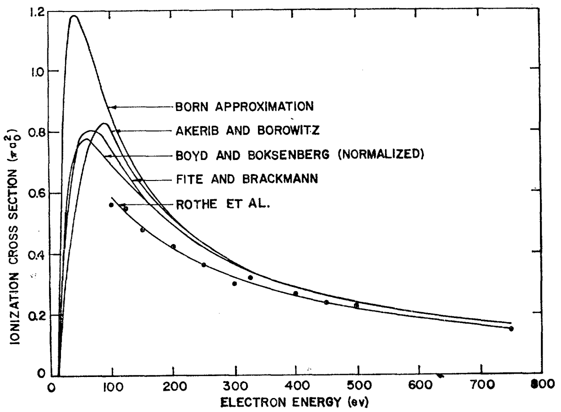


FIG. 10. Experimental and theoretical (impulse approximation[24a]) cross section for ionization of hydrogen atoms on electron impact.[24,25]

Rothe *et al.*[24] have repeated the absolute determination of the ionization cross section for electrons with energy from 100 to 750 eV. Their results, together with those of Boyd and Boksenberg[25] (Born normalized), are reproduced in Fig. 10,[24a] and are seen to be somewhat smaller than those of reference 22.

III. PARTIAL WAVE THEORY

(a) Introduction

In the center of gravity frame, the nonrelativistic Schrödinger equation for the interaction of electrons or positrons with hydrogen atoms is

$$\left[\frac{-\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)-\frac{e^2}{r_1}\pm\left(\frac{e^2}{r_2}-\frac{e^2}{r_{12}}\right)-E\right] \times \psi(\mathbf{r}_1,\mathbf{r}_2)=0\,,$$

where r_1 and r_2 are the coordinates of the atomic electron and impinging particle, respectively, relative to the (infinitely heavy) proton. The upper plus sign is used for incident positrons, the lower minus sign for incident electrons.

Since numerical calculations are generally performed with dimensionless independent variables, it is convenient to introduce atomic units at the outset. In these units, the Bohr radius of the hydrogen atom, $a_0\equiv\hbar^2/me^2=0.5\times10^{-8}$ cm., is taken to be the unit of length. Thus, on multiplying the Schrödinger equation by a_0^2, we obtain

$$\left[-\nabla_1^2-\nabla_2^2-\frac{2}{r_1}\pm2\left(\frac{1}{r_2}-\frac{1}{r_{12}}\right)-\mathcal{E}\right] \times \psi(\mathbf{r}_1,\mathbf{r}_2)=0\,, \quad \text{(III.1)}$$

where r_1 and r_2 are measured in units of a_0, and $\mathcal{E}\equiv E/(e^2/2a_0)$. Since the ground-state energy of the hydrogen atom $E_{\text{H}}=e^2/2a_0$, then $\mathcal{E}$ is measured in units of E_{H} (Rydbergs) i.e., 13.6 eV. All cross sections are given in units of πa_0^2.

The standard method for solving Eq. (III.1) is to expand the total wave function Ψ in terms of the eigenstates of the target Hamiltonian, i.e.,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\left(\sum\nolimits_\nu+\int d\nu\right)\psi_\nu(\mathbf{r})F_\nu(\mathbf{r}_\alpha)\,, \quad \text{(III.2)}$$

where, in Hartree units, the wave equation for the hydrogen atom is

$$(-\nabla^2-2/r-\epsilon_n)\psi_\nu(\mathbf{r})=0\,. \quad \text{(III.3)}$$

The integral symbol in Eq. (III.2) allows for integration over the continuous spectrum, $\epsilon>0$. We use the symbol ν to represent the three quantum numbers of the hydrogen atom nl_1m_1. Substituting Eq. (III.2) into Eq. (III.1) and using Eq. (III.3), gives a system of coupled equations for the "expansion coefficients" F_ν, which describes the relative motion of the incident (or emerging) projectile and target atom in a quantum state specified by ν:

$$[\nabla_\alpha^2+k_n^2]F_\nu(\mathbf{r}_\alpha)=\int d\mathbf{r}\psi_\nu^*(\mathbf{r})U\Psi(\mathbf{r},\mathbf{r}_\alpha)\,, \quad \text{(III.4)}$$

where $U\equiv\pm2(1/r_\alpha-1/r_{12})$. In Eqs. (III.2)–

---

[24] E. W. Rothe, L. L. Marino, R. H. Neynaber, and S. M. Trujillo, Phys. Rev. **125**, 582 (1962).

[24a] R. Akerib and S. Borowitz, Phys. Rev. **122**, 1177 (1961).

[25] R. L. F. Boyd and A. Boksenberg, *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases—Uppsala 1959.* (North-Holland Publishing Company, Amsterdam, 1960) Vol. I, p. 529.

(III.4) we have used $\mathbf{r}$ to denote the position vector of the atomic electron in order to avoid specifying which of the two identical electrons is in the atom, and $\mathbf{r}_\alpha$ to denote the position of the emerging particle. If the expansion (III.2) is substituted into the right-hand side of (III.4), then we obtain the system of equations

$$[\nabla_\alpha^2 + k_n^2]F_\nu(\mathbf{r}_\alpha) = [\textstyle\sum_{\nu'} + \int d\nu'] \, U_{\nu\nu'}F_{\nu'}(\mathbf{r}_\alpha) \,, \tag{III.5}$$

where

$$U_{\nu\nu'}(\mathbf{r}_\alpha) = \pm 2\int d\mathbf{r}\psi_\nu^*(\mathbf{r})\left[\frac{1}{r_\alpha} - \frac{1}{r_{12}}\right]\psi_{\nu'}(\mathbf{r}) \tag{III.6}$$

and

$$k_n^2 = (\mathcal{E} - \epsilon_n) \,. \tag{III.7}$$

The wave number k_n is measured in units of $a_0{}^{-1}$.

The expansion Eq. (III.2) and the method for obtaining the systems of equations (III.5), was suggested by Massey and Mohr[26] and has formed the basis for most wave mechanical scattering calculations for the last thirty years. For a review of the different approximations to Eq. (III.5) see reference 3.

The physics of the collision is inserted by obtaining only those solutions of Eq. (III.5) which satisfy certain prescribed boundary conditions. For example, when particle 2 is incident on the atom and neglecting long range forces (see Eq. III.9) below)

$$F_{\nu'}(\mathbf{r}_2) \underset{\mathbf{r}_2\to\infty}{\backsim} e^{i\mathbf{k}_{n'}\cdot\mathbf{r}_2}\delta_{\nu\nu'} + e^{ik_{n'}r_2}f_{\nu'\nu}(\hat{r}_2)/r_2 \,, \quad k_{n'}^2 > 0$$
$$\backsim e^{-|k_{m'}|r_2}g_{\nu'\nu}(\hat{r}_2)/r_2 \,, \quad k_{m'}^2 < 0 \,, \tag{III.8}$$

where the initial state of the target atom is denoted by ν. The amplitude $f_{\nu'\nu}(\hat{r}_2)$ is related to the cross section for a transition from state ν to state ν' (see reference 2, pp. 278–289). The normalization is chosen such that the incident plane wave has unit amplitude.

Castillejo, Percival, and Seaton[27] have used Eq. (III.5) as the basis for a quantum-mechanical derivation of the polarization potential. As the impinging particle approaches the atom from a large distance, the first force to become effective, between the atom and the projectile, is that due to the distortion (polarizability) of the electron charge distribution of the atom by the incident particle. For particles incident on the ground state of atomic hydrogen, and which do not possess enough energy to excite the atom, F_ν decays exponentially for $n > 1$. Thus, for large values of r_2, it might be possible to replace all the coupling terms, $\sum_{\nu'}U_{1\nu'}(r_2)F_{\nu'}(r_2)$, in Eq. (III.5) by a single diagonal potential term $U_p(r_2)F_{100}(\mathbf{r}_2)$, say. Here U_p represents the induced potential energy.

These authors[27] show that, for $n \neq 1$,

$$F_\nu(\mathbf{r}_2) \backsim \pm\tfrac{1}{2}U_{\nu,100}(\mathbf{r}_2)F_{100}(\mathbf{r}_2)/(k_1^2 - k_n^2) + O(r^{-3}) \,, \tag{III.9}$$

and so Eq. (III.5), for $\nu = 100$, becomes at large distances

$$\left(\nabla_2^2 + k_1^2\right)F_{100}(\mathbf{r}_2) \backsim \tfrac{1}{2}\sum_{\nu'\neq 1}\frac{U_{1\nu'}U_{\nu'1}}{k_1^2 - k_{n'}{}^2}F_{100}(\mathbf{r}_2)$$
$$+ O(\mathrm{r}^{-5}) \backsim U_p(\mathbf{r}_2)\,\mathrm{F}_{100}(\mathbf{r}_2) \,. \tag{III.10}$$

Hence, the polarization potential is given by

$$U_p(r_2) = \tfrac{1}{2}\sum_{\nu'\neq 1}\frac{|U_{\nu'1}|^2}{(k_1^2 - k_{n'}^2)} \backsim \alpha/r^4 \,, \tag{III.11}$$

where, for $n \neq 1$, and $l_1 = 1$

$$\alpha \equiv \tfrac{2}{3}\sum_{n\neq 1}\left|\int_0^\infty P_{n1}(r')r'P_{10}(r')dr'\right|^2$$
$$\div (\epsilon_n - \epsilon_1) = 4.5 \text{ for hydrogen.}$$

P_{nl_1}/r are the radial eigenfunctions of the hydrogen atom. We note that the $l_1 = 0$ contributions to $U_{\nu 1}$ vanish because of the orthogonality of the hydrogen wave functions. The form of the matrix element implies that this approximation is equivalent to the incident particle inducing a *dipole* moment in the atom. The contributions from higher multipoles has been considered by Temkin.[28] Using the matrix elements tabulated by Green, Rush, and Chandler,[29] Castillejo *et al.* showed that the $2P$ state contributes 65.8% of the polarizability. The importance of this long-range interaction becomes more apparent when we discuss details of calculations carried out at incident energies close to $k^2 = 0$.

If we expand F_ν in terms of surface harmonics

$$F_\nu(\mathbf{r}) = \sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2} f_{\nu l_2 m_2}(r)Y_{l_2 m_2}(\hat{r})/r \tag{III.12}$$

and substitute this expansion into Eq. (III.5) we obtain systems of an infinite number of coupled second-order differential equations

$$\left[\frac{d^2}{dr_2} + k_n^2 - \frac{l_2(l_2+1)}{r_2}\right]f_{\nu l_2 m_2}(r)$$
$$= r\int d\hat{r}Y_{l_2 m_2}^*(\hat{r})\sum_{\nu'}U_{\nu\nu'}F_{\nu'} \,, \tag{III.13}$$

---

[26] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A**136**, 289 (1932).

[27] L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc. (London) A**254**, 259 (1960).

[28] A. Temkin, Phys. Rev. **116**, 358 (1959); see also **107**, 1004 (1957).

[29] L. C. Green, P. P. Rush, and C. D. Chandler, Astrophys. J. Suppl. **3**, No. 26, 37 (1957).

where $f_{\nu,l_2=0,0}$ is the s-partial wave for the impinging electron when the atom is in the state ν; $f_{\nu,l_2=1,m_2}$ is the p-partial wave, etc. For $k_n^2 > 0$, the solutions to Eq. (III.13) have the asymptotic form

$$f_{\nu l_2 m_2} \backsim A_{\nu l_2 m_2} \sin (k_n r - l_2\pi/2 + \delta_{\nu l_2 m_2}) ,$$

where δ is the partial-wave phase shift.

Thus, in effect, we have expanded Ψ in a basis $\psi_{nl_1m_1}(\mathbf{r}_1) Y_{l_2m_2}(\hat{r}_2)$. Including the spin of the two electrons σ_1 and σ_2 gives the complete basis to be

$$\psi_{nl_1m_1}(\mathbf{r}_1) Y_{l_2m_2}(\hat{r}_2) \chi_{\frac{1}{2}m_1^s}(\sigma_1) \chi_{\frac{1}{2}m_2^s}(\sigma_2) \equiv \Psi_\gamma . \quad \text{(III.14)}$$

Therefore, the expansion of the over-all wave function is

$$\Psi(\mathbf{r}_1,\mathbf{r}_2;\sigma_1,\sigma_2) = \sum\nolimits_\gamma \Psi_\gamma(\mathbf{r}_1,\hat{r}_2;\sigma_1\sigma_2) f_\gamma(r_2)/r_2 . \quad \text{(III.15)}$$

In practical calculations, it is impossible to solve Eq. (III.13) exactly, since only a finite number of terms can be included in the expansion (III.2). If a truncated expansion is used, then Ψ_{trunc} is not a solution of the Schrödinger equation (III.1). This question is discussed in Mott and Massey[1] (pp. 141, 217, 260). We merely note that this difficulty arises because of the possibility that the incident electron may be captured into an atomic state and the atomic electron ejected; or the possibility of the incident positron capturing the atomic electron to form positronium. In both problems, the approximate Ψ will fail to satisfy necessary orthogonality relations.

Furthermore, even if we disregarded this orthogonality problem, Eq. (III.13) would still be an infinite coupled system if we included any nonspherical state of the hydrogen atom in the truncated eigenfunction expansion. Castillejo *et al.*[27] have raised another objection to using Eq. (III.2). They have shown that when the incident particle has kinetic energy too small for inelastic collisions to occur, then the integrand in the integral over the continuous spectrum contains a singularity.

An alternative procedure is to assume that the total wave function Ψ satisfies Hartree-Fock equations. Although this method is not entirely satisfactory [see Mott and Massey[1] (p. 218)], it has enjoyed great popularity.

(b) Cross Section Formulas

Before deriving the form of the continuous-state Hartree-Fock equations, we shall introduce the most convenient representation for describing this class of problems. We shall assume that the effects of the spin-orbit interaction can be neglected. Therefore, both the total orbital angular momentum, with quantum numbers L and M_L, and the total spin, S and M_S, are separately conserved during the collision. Furthermore, the over-all parity of the system will be conserved. Thus, a convenient representation to describe the collision will be one which is diagonal in $LM_LSM_S\pi$. This representation will be labeled $\Gamma = |k_nnl_1l_2LM_LSM_S\pi)$, where (k_nnl_2) can be identified with the channel index α of Blatt and Biedenharn.[30] The channel index specifies the type of incoming particle (electron, positron, positronium) and the quantum state of the target (hydrogen atom or proton). The state of the system (electron + hydrogen atom or positron + hydrogen atom) before the collision is described by the channel index $(k_{n'}n'l_1'l_2') \equiv \alpha'$, which we note includes the channel orbital angular momentum l_2', and the state after the collision is described by $(k_nnl_1l_2) \equiv \alpha$.

The method for deriving the cross section formulas has been given by Blatt and Biedenharn. We shall present the outline of the argument here. The most general wave function in channel $(k_nnl_1l_2)$ with total quantum numbers LM_LSM_S consists of the superposition of an ingoing and outgoing spherical wave:

$$\Psi_{\alpha LM_LSM_S}(\mathbf{r}_1,\mathbf{r}_2;\sigma_1,\sigma_2) \backsim \frac{1}{r_\alpha k_\alpha{}^{1/2}} \mathcal{Y}_{Ll_1l_2}^{M_L} \chi_S^{M_S} \phi_\alpha \times \{A_\alpha^{LM_LSM_S} \exp[-i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)] - B_\alpha^{LM_LSM_S} \exp[i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)]\} , \quad \text{(III.16)}$$

where the incident beam is normalized to unit *flux*, and where ϕ_α is the product of the wave function of the target and the internal state of the incident particle. For positronium incident on protons, r_α is identified with $\mathbf{R} \equiv (\mathbf{r}_1 + \mathbf{r}_2)/2$. If the amplitudes A_α of the ingoing waves are known, then the amplitudes B_α of the outgoing waves are determined uniquely by the wave equation. The relation between A_α and B_α defines the *scattering matrix*

$$B_{\alpha'}^{LM_LSM_S} \equiv \sum\nolimits_\alpha S_{\alpha'\alpha}^{LS} A_\alpha^{LM_LSM_S} , \quad \text{(III.17)}$$

where the matrices $S_{\alpha'\alpha}^{LS}$ are independent of M_L and M_S (see reference 30). The sum over α in Eq. (III.17) is taken over all the incident channels. Substituting Eq. (III.17) into (III.16) gives

$$\Psi_{\alpha LM_LSM_S} \backsim (1/r_\alpha k_\alpha^{1/2}) \mathcal{Y}_{Ll_1l_2}^{M_L} \chi_S^{M_S} \phi_\alpha \sum\nolimits_{\alpha'} A_{\alpha'}^{LM_LSM_S} \times \{\delta_{\alpha\alpha'} \exp[-i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)] - S_{\alpha\alpha'}^{LS} \exp[i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)]\} . \quad \text{(III.18)}$$

The asymptotic form of the total wave function

---

[30] J. M. Blatt and L. C. Biedenharn, Revs. Modern Phys. **24**, 258 (1952); also see the correction pointed out by R. Huby, Proc. Phys. Soc. (London) A67, 1103 (1954).

of the system, $\Psi \equiv \sum_\Gamma \Psi_\Gamma$ for the system initially in state $n'l_1'$ is

$$\Psi^{(n'l_1')} \backsim \sum_\Gamma \sum_{l_2'} (1/r_\alpha k^{1/2}{}_\alpha) \mathcal{Y}_{Ll_1l_2}^{M_L} \chi_S^{M_S} \phi_\alpha A_{\alpha'}{}^{LM_LSM_S} \times \{\delta_{\alpha\alpha'} \exp[-i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)] - S_{\alpha\alpha'}^{LS} \exp[i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)]\} . \quad \text{(III.19)}$$

Equation (III.19) suggests that the wave function for the whole system, initially in state Γ', be taken to be of the form

$$\Psi^{\Gamma'}(\mathbf{r}_1\mathbf{r}_2,\sigma_1\sigma_2) = \sum_\Gamma (1/r_\alpha k^{1/2}{}_\alpha) \mathcal{Y}_{Ll_1l_2}^{M_L}(\hat{r},\hat{r}_\alpha) \times \chi_S^{M_S}(\sigma_1\sigma_2)\phi_\alpha F_\Gamma^{\Gamma'}(r_\alpha) , \quad \text{(III.20)}$$

where the new expansion coefficients have the asymptotic form

$$F_\Gamma^{\Gamma'}(r_\alpha) \backsim A_{\alpha\alpha'}^{LM_LSM_S}\{\delta_{\alpha\alpha'} \exp[-i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)] - S_{\alpha\alpha'}^{LS} \exp[i(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)]\} . \quad \text{(III.21)}$$

Since it is more convenient to work with the real and symmetric $\mathcal{R}$ matrix[31] than the S matrix in numerical calculations, where

$$S \equiv (1 + i\mathcal{R})/(1 - i\mathcal{R}) , \quad \text{(III.22)}$$

we write

$$F_\Gamma^{\Gamma'}(r_\alpha) \backsim C_\Gamma^{\Gamma'}\{(1/k_\alpha) \sin(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi) + \mathcal{R}_{\alpha\alpha'}^{LS}(1/k_\alpha) \cos(k_\alpha r_\alpha - \tfrac{1}{2} l_2\pi)\} \quad \text{(III.23)}$$

where

$$C_\Gamma^{\Gamma'} = -2ik_\alpha A_{\alpha\alpha'}^{LM_LSM_S}/(1 - i\mathcal{R}_{\alpha\alpha'}^{LS}) . \quad \text{(III.24)}$$

In the case of electrons incident on hydrogen atoms, the S-matrix elements for the total spin zero and one states are different. This difference is due to the requirements of the Pauli principle, which demands that the wave function of the electron hydrogen system be antisymmetric in the coordinates of the bound and free electrons. The spin symmetric state has associated with it, therefore, an antisymmetric space wave function; the spin antisymmetric state has associated with it a symmetric space wave function. For this reason the electrons will, on the average, move in different regions of the potentials in different spin states and consequently experience different scattering.

It was shown by Burke and Schey[32] that in the representation in which the spin of each electron and its Z component are diagonal, the scattering amplitude can be written

$$M(\theta\phi) = \tfrac{1}{4}[3F(\theta\phi) + G(\theta\phi)] + \tfrac{1}{4}[F(\theta\phi) - G(\theta\phi)]\, \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 , \quad \text{(III.25)}$$

where σ_1 and σ_2 are the usual Pauli spin matrices for electrons 1 and 2, respectively, and the outer product of the σ matrices is taken in the second term on the right-hand side. The functions $F(\theta\phi)$ and $G(\theta\phi)$ are the triplet, $S = 1$, and singlet, $S = 0$, amplitudes, which in the case of an atomic transition from level $n'l_1'm'$ to nl_1m are given by

$$A_S(\theta\phi) = \frac{1}{2k_{n'}} \sum_{Ll_2l_2'} [\pi(2l_2' + 1)]^{\frac{1}{2}} (l_1'l_2'm'0|Lm') \times (l_1l_2m\, m' - m|Lm') T_{\alpha\alpha'}^{LS} Y_{l_2m'-m}(\theta\phi) , \quad \text{(III.26)}$$

where $S = 1 - iT$. In the case of positrons incident on hydrogen atoms, $F(\theta\phi) = G(\theta\phi)$ and the scattering amplitude $M(\theta,\phi)$ becomes spin independent.

We introduce the density matrix of the system discussed in detail by Fano[33] by

$$\rho = \tfrac{1}{4}(1 + \textstyle\sum_i P_i^{(1)}\sigma_1^i + \sum_i P_i^{(2)}\sigma_2^i + \sum_{ij} Q_{ij}\sigma_1^i\sigma_2^j) , \quad \text{(III.27)}$$

where the polarization vectors $P_i^{(1)}$ and $P_i^{(2)}$ are the expectation values of the spins of electrons 1 and 2, respectively, and the correlation tensor Q_{ij} is the expectation value of the product of the spins of electrons 1 and 2.

The density matrix ρ_f after scattering is related to the density matrix ρ_i before scattering by

$$\rho_f = [1/(2l_1 + 1)] \textstyle\sum_{mm'} M(\theta\phi)\rho_i M(\theta\phi)^\dagger . \quad \text{(III.28)}$$

The polarization and the correlation tensor, after scattering, are given by

$$\begin{aligned} P_i^{(1)}(\theta) &= \mathrm{Tr}(\rho_f\sigma_1^i)/\mathrm{Tr}(\rho_f) \\ P_i^{(2)}(\theta) &= \mathrm{Tr}\,(\rho_f\sigma_2^i)/\,\mathrm{Tr}\,(\rho_f) \\ Q_{ij}(\theta) &= \mathrm{Tr}\,(\rho_f\sigma_1^i\sigma_2^j)/\,\mathrm{Tr}\,(\rho_f) \end{aligned} \quad \text{(III.29)}$$

and can then be expressed in terms of the corresponding quantities before scattering together with the triplet and singlet amplitudes.

The differential cross section is given by

$$\sigma(\theta) = \mathrm{Tr}\,(\rho_f) = \tfrac{1}{4}[1/(2l_1 + 1)] \textstyle\sum_{mm'} \times [3|F(\theta\phi)|^2 + |G(\theta\phi)|^2] . \quad \text{(III.30)}$$

We now observe that at each energy and scattering angle, a transition from level $n'l_1'$ to level nl_1 can be

---

[31] E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947); J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York), 1952.

[32] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 163 (1962).

[33] U. Fano, Revs. Modern Phys. **29**, 74 (1957).

expressed in terms of three parameters, the magnitudes of the triplet and singlet amplitudes and their relative phase, for electron-hydrogen atom scattering; and one parameter, the magnitude of the triplet *or* singlet amplitude, for positron-hydrogen atom scattering. In order to specify the scattering completely, therefore, three independent experiments at each energy and angle must be carried out with electrons, whereas only one, the differential cross section, will suffice with positrons.

The explicit derivation of the cross section formulas of interest here follows that given in Blatt and Biedenharn with the necessary changes made. The explicit forms have been given by Percival and Seaton[34] and we quote their results below. The total cross section for transitions from level $n'l_1'$ to level nl_1 is (in units of πa_0^2)

$$Q(n'l_1' \rightarrow nl_1) = \sum_{SLl_2l_2'} \frac{(2L+1)(2S+1)}{4k_{n'}^2(2l_1'+1)} |T_{\alpha,\alpha'}^{LS}|^2 . \qquad \text{(III.31)}$$

The differential cross section for transitions between the two levels is (in units of πa_0^2)

$$\begin{aligned} I(n'l_1' \rightarrow nl_1;\theta) = {} & \sum_{\lambda} P_\gamma(\cos\theta) \frac{(-1)^{l_1'+l_1}}{16k_{n'}^2(2l_1'+1)\pi} \\ & \times \sum_S (2S+1) \sum_{LL'} \sum_{p_2p_2'} \sum_{l_2l_2'} \\ & \times Z(l_2Lp_2L';l_1\lambda)\, Z(l_2'Lp_2'L';l_1'\lambda) \\ & \times T_{nl_1l_2,n'l_1'l_2'}^{LS} T_{nl_1p_2,n'l_1'p_2'}^{L'S*} , \end{aligned} \qquad \text{(III.32)}$$

Where the Z coefficients are defined in reference 30.

We note that (nl_1) in the above formulas can designate either the states of atomic hydrogen or positronium. Therefore, it is possible to calculate the following from these formulas:

(a) the elastic-scattering cross sections of electrons and positrons on hydrogen atoms, as well as positronium on protons,
(b) the excitation and de-excitation cross sections among the levels of the two atomic systems, and
(c) the cross section for positronium formation and quenching.

At this point it is convenient to present the expressions for $Q(1s \rightarrow 2pm_1)$ which Percival and Seaton[35] have shown to be related to P, the fractional polarization of Lyman-α radiation emitted perpendicular to the direction of the incident beam. It is recalled that P is important for measuring $Q(1s\text{-}2p)$.

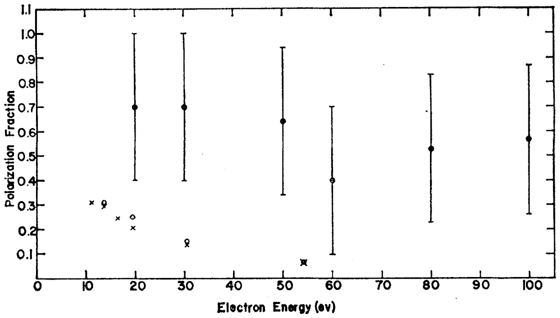


FIG. 11. Polarization fraction for Lyman - α radiation from e^-H collisions. Lines with error bars are experimental determinations,[15] circles[60] and crosses[66] are preliminary theoretical estimates; more recent values are given in Table XV.

Fite and Brackmann[15] have measured P as a function of the incident electron energy; their results are given in Fig. 11. Percival and Seaton show that

$$P \approx 3(1-x)/(7+11x) , \qquad \text{(III.33)}$$

where $x \equiv Q(1s \rightarrow 2p \pm 1)/Q(1s \rightarrow 2p0)$ and, in units of πa_0^2,

$$\begin{aligned} Q^S(1s \rightarrow 2pm) = {} & \frac{1}{k_1^2} \sum_{l,L,L'} [(2L+1)(2L'+1)]^{1/2} \\ & \times T_{21l;10L}^{LS} T_{21l;10L'}^{L'S*} (1lm-m|L0)(1lm-m|L'0) \end{aligned} \qquad \text{(III.34)}$$

(c) Hartree-Fock Equations

The importance of the Hartree-Fock equations is due to their connection with variational principles for the parameters required in the calculation of cross sections, see Hulthén[36] and Kohn.[37] We shall demonstrate this connection in the following paragraphs, but we shall defer a detailed discussion on variational principles to Sec. V. We merely remark here that the method is of particular importance when there is no bound state of the over-all system (projectile plus target atom), since the calculations then yield an upper bound on the scattering length A, from which a bound on the cross section can be deduced if $A < 0$. Even if a composite bound state does exist, provided some variationally determined information is available on the wave function and energy of the composite bound state, then its contribution may be subtracted and a bound on the scattering length still obtained.

To find the required variational principle, it is noted that the exact wave functions have the property that

$$I' \equiv \int \Psi_T^*(\mathbf{r}_1,\hat{r}_2;\sigma_1\sigma_2)(H-E)\Psi(\mathbf{r}_1\mathbf{r}_2;\sigma_1\sigma_2)d\mathbf{r}_1 d\mathbf{r}_2 = 0 . \qquad \text{(III.35)}$$

---

[34] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. **53**, 654 (1957).

[35] I. C. Percival and M. J. Seaton, Trans. Roy. Soc. (London) A**251**, 113 (1958).

[36] L. Hulthén, Kgl. Fysiograf. Sällskap. Lund, Forh. **14**, No. 21 (1944); Arkiv. Mat. Astr. Fys. **35a**, 25 (1948).

[37] W. Kohn, Phys. Rev. **74**, 1763 (1948).

The approximate calculation of the total wave function is based on the following considerations.

Let us assume that we can construct approximate trial functions Ψ_t, which satisfy the true boundary conditions. In particular, Ψ_t has the desired asymptotic form (III.20) and (III.23), although the coefficients $\mathcal{R}_{\alpha\alpha'}$ may be in error. Since the Hamiltonian H is diagonal in LM_LSM_S, it is possible to consider the individual terms of Eq. (III.35):

$$I^{LM_LSM_S} \equiv I = \int \Psi_\Gamma^*(H - E)\Psi_{\alpha' LM_LSM_S} d\mathbf{r}_1 d\mathbf{r}_2 = 0\,. \tag{III.36}$$

For small arbitrary variations of the type

$$\begin{aligned}\delta\Psi \equiv \Psi_t - \Psi &= \Psi_\Gamma(\mathbf{r},\hat{r}_\alpha;\sigma_1\sigma_2)\delta F_\Gamma^{\Gamma'}(r_\alpha)/(k_\alpha r_\alpha)\\ &\backsim \Psi_\Gamma \quad C_\Gamma^{\Gamma'} \cos\,(k_\alpha r_\alpha - l_2\pi/2)\delta\mathcal{R}_{\alpha\alpha'}^{LS}/(k_\alpha r_\alpha)\end{aligned} \tag{III.37}$$

about the true total wave function Ψ, the first variation of I is given by

$$\delta I = \int \Psi(H\text{-}E)\delta\Psi dv + \int \delta\Psi(H\text{-}E)\delta\Psi dv\,,$$

where $dv = d\mathbf{r}_1 d\mathbf{r}_2$. Using Green's theorem to reduce the first term on the right-hand side of this equation we obtain (see reference 2, p. 259 for the one-dimensional case)

$$\begin{aligned}\delta I = &-\tfrac{1}{2}\int ds\left[F(\mathbf{r})\frac{\partial}{\partial n}\delta F(\mathbf{r}) - \delta F(\mathbf{r})\frac{\partial}{\partial n}F(\mathbf{r})\right]\\ &+ \int \delta\Psi(H - E)\delta\Psi dv\,,\end{aligned}$$

where n is normal to the surface s ($\equiv r^2 d\hat{r}$) over which the integral is performed. Hence,

$$\delta I = C^2\delta\mathcal{R}/2k + \int \delta\Psi(H - E)\delta\Psi dv\,. \tag{III.38}$$

Neglecting the term in $\delta\Psi^2$, then

$$\delta(I - C^2\mathcal{R}/2k) = 0 \tag{III.39}$$

provides the basis for a variational principle since the quantity $(I\text{-}C^2\mathcal{R}/2k)$ is stationary with respect to the variations considered. Writing $\delta I = I_t - I$ and $\delta\mathcal{R} = \mathcal{R}_t - \mathcal{R}$, then up to second order in the error in the wave function

$$\mathcal{R} = \mathcal{R}_t - 2I_t k/C^2\,. \tag{III.40}$$

In the eigenfunction expansion approach, the trial functions $F_t(r)$ are chosen such that $I_t = 0$. Hence, the true value of the elements of the $\mathcal{R}$ matrix are given by $\mathcal{R}_t$ up to $(\delta\Psi)$.[2] The question of the error involved will be discussed in Sec. V.

In the electron problem, Percival and Seaton have assumed an antisymmetrized linear combination of Eq. (III.20), namely,

$$\Psi^{\Gamma'} = (1/\sqrt{2})(1 - P_{12})\textstyle\sum_\Gamma \Psi_\Gamma(\mathbf{r},\hat{r}_\alpha;\sigma_1\sigma_2)F_\Gamma^{\Gamma'}(r_\alpha)/r_\alpha\,, \tag{III.41}$$

where P_{12} interchanges all the coordinates of the incident particle and atomic electron. This explicitly symmetrized function, which formally still involves an integral over the continuum states, does not have a singularity in the integrand.[27]

We should like to make a few remarks about the continuum in Eqs. (III.2) and (III.41). Since the former is a precise mathematical expansion, it *includes* allowance for the physical processes of electron exchange in the e^-H problem and positronium formation in the e^+H problem. Mathematically, these processes are "constructed" from those terms in Eq. (III.2) for which $k_n^2 < 0$, including the continuum. However, due to the unresolved technical difficulties in handling the continuum, Eq. (III.2) is not a convenient expansion for examining the rearrangement processes. The simplest way to include these processes is to rewrite Eq. (III.2) as the sum of two terms. The first term is a finite sum of discrete states, while the second term $R(\mathbf{r}_1,\mathbf{r}_2)$, is the remainder. This remainder can then be expanded in terms of the eigenfunctions with argument $\mathbf{r}_2$, (or ρ in the e^+H problem)! The amplitudes of the expansion coefficients are related directly to the cross sections for the rearrangement processes. Even though only a few of the discrete states may be retained in this second expansion, by including them we have made some allowance for the continuum. In practical applications of Eq. (III.41), no attempt has been made to include the continuum other than implicitly as described above.

In the positron problem, Smith[38] has assumed Eq. (III.20), where the sum extends over the discrete states of positronium as well as those of the hydrogen atom. To avoid confusion in notation in the positron problem, Eq. (III.20) can be written

$$\begin{aligned}\Psi^{\Gamma'} = &\sum_\Gamma \Psi_\Gamma(\mathbf{r}_1\hat{r}_2,\sigma_1\sigma_2)\,\frac{F_\Gamma^{\Gamma'}(r_2)}{r_2}\\ &+ \sum_\Delta \Psi_\Delta(\mathbf{p}\hat{R}\sigma_1\sigma_2)\,\frac{G_\Delta^\Gamma(R)}{R}\,,\end{aligned} \tag{III.42}$$

where $\Delta = (k_m m p_1 p_2 LM_LSM_S)$ and mp_1 represents the principal and orbital quantum numbers of the states of positronium. The asymptotic forms of F and G are given by Eq. (III.23).

If the variations in the functions F and G are

---

[38] K. Smith, Proc. Phys. Soc. (London) **78**, 549 (1961).

allowed to be completely arbitrary apart from the boundary conditions (III.23) and the continuity requirements of the functions and derivatives, then Eq. (III.35) leads to Euler-Lagrange equations which are a set of ordinary coupled second-order integro-differential equations which the F and G functions must satisfy. For the electron-hydrogen atom scattering problems these equations are

$$\left[\frac{d^2}{dr^2} - \frac{l_2(l_2+1)}{r^2} + k_n^2\right] F_\nu^{LS}(r) = \sum_{\nu'} \left[V_{\nu\nu'}^{L} - W_{\nu\nu'}^{LS}\right] F_{\nu'}^{LS}(r)\,, \tag{III.43}$$

where all the quantities are defined by Percival and Seaton.[34] In the positron problem they are

$$\left[\frac{d^2}{dr^2} - \frac{l_2(l_2+1)}{r^2} + k_n^2\right] F_\nu^{LS}(r) = \sum_{\nu'} V_{\nu\nu'}^{L}(r) F_{\nu'}(r) + \sum_{\mu'} \int_0^\infty K_{\nu\mu'}^{L}(r,R) G_{\mu'}(R)\,dR\,,$$

$$\left[\frac{d^2}{dR^2} - \frac{p_2(p_2+1)}{R^2} + k_m^2\right] G_\mu^{LS}(R) = \sum_{\mu'} V_{\mu\mu'}^{L}(R) G_{\mu'}(R) + \sum_{\nu'} \int_0^\infty K_{\mu\nu'}(R,r) F_{\nu'}(r)\,dt\,, \tag{III.44}$$

where all the quantities are defined by Smith.[38]

These equations are the Hartree-Fock equations for the scattering problem. Since the form of these equations is independent of the boundary conditions, we have omitted the incident index Γ' in writing these equations. From a complete set of solutions to these equations an appropriate linear combination can be taken and any element of the $\mathcal{R}$ matrix evaluated. It is obvious that any solution to these equations satisfies the Kohn variational principle (III.40) with the integral term zero.

Most of the methods which have been tried in the low-energy scattering problem can be related to each other within the framework of the above discussion. In particular, the various approximations are usually different truncations of Eqs. (III.43) and (III.44). These are discussed in Sec. IV.

(d) Effective-Range Theory

The purpose of inserting this subsection here, rather than in Sec. VI, is to introduce the concept of scattering length, which will play an important role in this review. In Sec. V (b) we discuss the problem of estimating rigorous upper and lower bounds on the elements of the $\mathcal{R}$ matrix. Since most of this work has been done at zero energy, it is important that the various approximations used in scattering problems give scattering lengths within the estimated bounds.

The effective range theory[39] has proved useful in the analysis of low-energy nucleon-nucleon scattering data. According to this theory, $k \cot \delta_0$ (where δ_0 is the s-partial wave phase shift) can be expanded, in powers of k^2, as follows:

$$k \cot \delta_0 = -1/A + k^2 r_0/2 + O(k^4)\,, \tag{III.45}$$

where A is the scattering length and r_0 is the effective range. Borowitz and Greenberg[40] were the first to apply this theory to atomic collision problems. Its applicability to the scattering of an electron (or positron) by an atom has been examined in detail by O'Malley *et al.*[41] The basic assumption of the theory is that of the optical model, see Sec. VI (d), which asserts that the projectile-atom problem can be simulated by an equivalent one-body problem.

$$[d^2/dr^2 + k^2 - L(L+1)/r^2 - V(r)]u(r) = 0\,. \tag{III.46}$$

If $V(r)$ is a short-range optical potential, then $u(r)$ must tend, asymptotically, to a linear combination of the "free" solutions

$$u(k,0) = 0;\quad u(k,r) \backsim [krj_l(kr)] - \mathcal{R}^L[krn_l(kr)]\,, \tag{III.47}$$

where j and n are the spherical Bessel and Neumann functions, respectively.[42] For $k = 0$, $u(0,r)$ should approach a linear combination of the $k = 0$ free solutions, r^{L+1} and r^{-L}, for example

$$u(0,r) \backsim -r^{L+1} + (2L+1)!!(2L-1)!!A^L r^{-L} \tag{III.48}$$

which it does, provided

$$\lim_{k\to 0} \mathcal{R}^L/k^{2L+1} \equiv -A^L\,. \tag{III.49}$$

Here A^L is defined to be the *scattering length* for the Lth partial wave.

If the scattering length can be defined by Eq. (III.49), then expanding about zero energy, it is possible to derive the identity (for $L = 0$)[39]

$$-\mathcal{R}/k = A + k^2 \int_0^\infty (vv_0 - uu_0)dr\,, \tag{III.50}$$

---

[39] J. M. Blatt and J. D. Jackson, Phys. Rev. **76**, 18 (1949); H. A. Bethe, *ibid.* **76**, 38 (1949).

[40] S. Borowitz and H. Greenberg, Phys. Rev. **108**, 716 (1957).

[41] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961); Phys. Rev. **125**, 1300 (1962).

[42] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd Ed.

where v and v_0 are the solutions of the free Schrödinger equation for k^2 and $k^2 = 0$, respectively. However, the effective range, r_0, as defined by

$$r_0 \equiv 2\int_0^\infty (v_0^2 - u_0^2)dr \qquad \text{(III.51)}$$

has been shown by O'Malley *et al.* to be infinite for potentials which are of interest here, see Eq. (III.11). Hence the usual expansion (III.45) breaks down.

If $V(r)$ has a long range term, β_n^2/r^n, say, then Eq. (III.46) has the two independent solutions

$$r^{1/2}J_{(2L+1)/(n-2)}(x) \text{ and } r^{1/2}N_{(2L+1)/(n-2)}(x)\ , \qquad \text{(III.52)}$$

where $x = 2\beta_n r^{-(n-2)/2}/(n-2)$. For $n > 2L + 3$, the leading terms in the asymptotic form are the same as (III.48), but for $n \leqslant 2L + 3$, other terms appear in the asymptotic form and A^L, as defined by Eq. (III.49), does not exist.

O'Malley *et al.* modify the effective-range theory by taking out the long-range tail from $V(r)$ by writing

$$V(r) \equiv \Delta V(r) - \beta^2/r^n\ , \qquad \text{(III.53)}$$

where ΔV is a short-range potential which vanishes asymptotically faster than any inverse power of r. Then, the asymptotic form of $u(r)$ is taken to be a linear combination of the solutions (III.52). The relative amplitude of these two terms, denoted B, which is fixed by the requirement that $u(0) = 0$, determines the $\mathcal{R}$ matrix (i.e., $\tan\eta$).[41] Following Bethe's[39] analysis, the modified form of (III.50) is readily found to be

$$(B/\beta) \approx (B_0/\beta) + k^2\int_0^\infty (v_p v_{p0} - uu_0)dr\ , \qquad \text{(III.54)}$$

where the suffix p denotes the solution to the polarizability equation, see Eqs. (III.10) and (III.11), and

$$\lim_{k\to 0} \mathcal{R} \equiv -A = \beta/B_0\ . \qquad \text{(III.55)}$$

The modified form of (III.37) becomes[41] for $l = 0$

$$k\cot\eta = -1/A + \pi\beta^2 k/3A^2 + O(k^2\ln k)\ , \qquad \text{(III.56)}$$

while the total cross section is given by

$$\sigma = 4\pi A^2 + (8/3)\pi^2\beta^2 A k^2 + \cdots\ . \qquad \text{(III.57)}$$

In conclusion, we note that for $\beta^2 = 4.5$, the approximation is limited to energies *below* 1.5 eV.

In order to avoid confusion with respect to the sign of the scattering length, we shall adopt Schiff's[42] convention. That is, for repulsive forces ($V > 0$), which "push out" the wave function, we shall define the resulting phase shift to be negative ($\delta < 0$) and the scattering length to be positive. For an attractive potential, the sign of the scattering length will depend on the existence of bound states.

IV. APPROXIMATION SCHEMES

(a) Static Approximation

When only the $1S$ state of atomic hydrogen is taken in the expansion (III.41), the radial equations for the electron problem (III.43) uncouple and reduce to the following integro-differential equation,

$$[d^2/dr^2 - l(l+1)/r^2 + k^2]F^{lS}(r) = 2[\pm V^l(r) - W^{lS}]F^{lS}(r)\ . \qquad \text{(IV.1)}$$

This approximation is called the *static exchange approximation*. In the positron problem, Eqs. (III.44) reduce to the second-order differential equation (lower minus sign)

$$[d^2/dr^2 - l(l+1)/r^2 + k^2 \pm 2(1 + 1/r)e^{-2r}] \times F^l(r) = 0\ . \qquad \text{(IV.2)}$$

If the electron exchange is neglected, then Eq. (IV.1) reduces to (IV.2) with the upper plus sign. This approximation is called the *static or one-body approximation.*

Electrons: MacDougall[43] has solved Eq. (IV.2) for $l = 0$ and $k \leqslant 5$; Chandrasekhar and Breen[44] have solved Eq. (IV.2) for $l = 0$ and $l = 1$ with $k^2 \leqslant 1.75$; Smith, Miller, and Mumford[45] have solved this equation for $k = 1.0$, 1.2, 1.5, and 2.0 for all significant partial waves; John[46] has solved Eq. (IV.2) for $l = 0$, 1, and 2 for $k^2 \leqslant 1.0$. The phase shifts are given in Table I. All phase shifts in this review are given in radians.

The first solutions to the integro-differential Eq. (IV.1) were obtained by Morse and Allis.[47] However, Seaton[48] has pointed out that incorrect equations were used in the $l = 0$ calculations of reference 47. Ochkur[49] has solved Eq. (IV.1) for $l = 0$ and $k \leqslant 2.0$; John[46] has carried out careful numerical calculations in this approximation, having solved this equation for $l = 0$, 1, and 2 for $k^2 \leqslant 1.0$. The

---

[43] J. MacDougall, Proc. Roy. Soc. (London) **A136**, 549 (1933).

[44] S. Chandrasekhar and F. H. Breen, Astrophys. J. **103**, 41 (1946).

[45] K. Smith, W. F. Miller, and A. J. P. Mumford, Proc. Phys. Soc. (London) **76**, 559 (1960).

[46] T. L. John, Proc. Phys. Soc. (London) **76**, 532 (1960).

[47] P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

[48] M. J. Seaton, Proc. Roy. Soc. (London) **A241**, 522 (1957); see also J. Uretsky, M.S. Thesis, M.I.T. (1952).

[49] V. I. Ochkur, Vestnik Leningrad Univ. **4**, 53 (1958).

$l = 0$ and 1 phase shifts have been calculated also by Omidvar[50]; and $l = 2$ by McEachran and Fraser.[51] The phase shifts are given in Table II.

Whenever a single atomic state is assumed in the eigenfunction expansion, one has to solve equations of the form of (IV.1) and (IV.2). Smith *et al.*[45] have solved the equivalent to Eq. (IV.2) for the $2S$ and $3S$ states, for all significant l, whereas Ochkur[49] has solved the equivalent to (IV.1) for s waves ($l = 0$) for $2S$, $2P$, $3S$, $3P$, $3D$, $4S$, and $4D$.

TABLE I. Electron-hydrogen atom partial wave phase shifts (neglecting exchange). Row a: static approximation; row b: strong coupling; row c: 1*s*-2*s*-2*p*.

k^2 \ l		0	1	2
0.80	a	0.9356	0.0924	
0.74	b	0.9711		
	c	4.0358		
0.73	b	0.9521		
	c	3.9032		
0.7225	b	0.9431		
0.7	a	0.9527	0.0818	
	c	1.1244	3.2831	0.0630
0.6912	b	0.9202		
0.64	a	0.9633	0.0752	0.0087
	b	0.8962	0.0927	0.0095
0.522	b	0.8331		
0.5	a	0.9909	0.0584	0.0056
	c	0.8605	3.2282	0.0365
0.49	b	0.8071		
0.4191	b	0.7194	0.0558	
0.36	a	1.0210	0.0406	0.0030
	b	0.5887	0.0464	0.0032
0.2794	b	0.2305	0.0039	
0.25	a	1.0448	0.0260	0.0014
	b	0.0238	0.0294	
	c	0.0405	3.0402	
0.16	a	1.0575	0.0147	0.0005
	b	2.4960	0.0163	0.0006
0.09	a	1.0458	0.0066	
	b	2.2640		
0.04	a	0.9731	0.0021	
	b	2.3172	0.0023	
	c	2.3863		
0.01	a	0.721	0.0003	
	b	2.6015	0.0003	
	c	2.6739	0.0055	
0.0056	b	2.715		
0.0025	a	0.434		
	b	2.845		
0.0001	b	3.080		
0.0	a	(9.45)		
	b	(6.135)		
	c	(5.036)		

TABLE II. Electron-hydrogen atom partial wave phase shifts in the singlet and triplet spin states. Rows a, b, and c have the same significance as in Table I.

k^2 \ l		0		1		2	
		s	t	s	t	s	t
0.745	c	3.8751					
0.74	a	0.6087	1.541	−0.1159	0.3362	−0.0155	0.0395
	b	0.7318	1.540	−0.111	0.42		
	c	3.8560	. . .	0.904	3.5380	0.1329	0.0624
0.73	a	0.6124	1.548	−0.1160	0.3349	−0.0154	0.0388
	b	0.7004	1.5493				
	c	3.8192					
0.70	c	1.2396	1.5846	−0.0496	0.4159	0.0770	0.0594
0.64	a	0.651	1.614	−0.116	0.321	−0.0139	0.0327
	b	0.698	1.616	−0.114	0.3608	−0.0138	0.0366
0.5	a	0.7370	1.739	−0.1084	0.2866	−0.0108	0.0230
	c	0.8101	1.7568	−0.0585	0.3565	0.0424	0.0444
0.4	a	0.8248	1.849	−0.0778	0.2500		
	c	0.8876	1.870	−0.0511	0.3208	0.0332	0.0366
0.3	a	0.9488	1.987	−0.0811	0.2000		
	c	1.0084	2.0108	−0.0374	0.2696	0.0249	0.0283
0.25	a	1.031	2.070	−0.0702	0.1692	−0.0039	0.0070
	b	1.046	2.0704	−0.0646	0.2105	−0.0038	0.0081
	c	1.0820	2.0956				
0.16	a	1.239	2.257	−0.046	0.105	−0.0017	0.0029
	b	1.257	2.2575	−0.038	0.142		
0.09	a	1.508	2.461	−0.024	0.052	−0.0005	0.0008
	b	1.519	2.461	−0.0162	0.0771		
0.04	a	1.871	2.679	−0.0084	0.0166		
	b	1.8776	2.680	−0.0040	0.0281		
	c	1.9742	2.715				
0.01	a	2.396	2.908	−0.0012	0.0022		
	b	2.404	2.901	−0.0003	0.0040		
	c	2.491	2.9355	0.0041	0.0079	0.0009	0.0009
0.0	a	8.095	2.350				
	b	8.05	2.33				
	c	6.7418	1.8931				

Positrons: Massey and Moussa[52] have solved Eq. (IV.2) for $l = 0$ for $k = 0.2, 0.5$, and 1.0. These results have been checked by Smith *et al.*,[45] who solved this equation for $k = 1.0, 1.2, 1.5$, and 2.0 for all significant partial-wave contributions to the elastic scattering cross section. These latter authors also solved the analogous equation to (IV.2) for $2S$ and $3S$ states. The phase shifts are given in Table III.

Equations (IV.1) and (IV.2) represent scattering in a single channel. Therefore, we require those solutions which satisfy the boundary conditions, see (III.8),

$$F^l(0) = 0 \,.$$

$$F^l(r) \backsim i^l(2l+1)\sin(kr - l\pi/2)/k + c_l e^{ikr}, \tag{IV.3}$$

where $c_l = (2l+1)(e^{2i\delta_l} - 1)/2ik$. The partial-wave phase shifts, δ_l, are related to the $\mathcal{R}$ matrix by

$$\mathcal{R}_{ll} = \tan\delta_l$$

---

[50] K. Omidvar, Research Report No. CX-37 (1959), Division of Electromagnetic Research, New York University.

[51] R. P. McEachran and P. A. Fraser, Can. J. Phys. **38**, 317 (1960).

[52] H. S. W. Massey and A. H. A. Moussa, Proc. Phys. Soc. (London) **72**, 38 (1958).

The cross section formulas Eqs. (III.31) reduce to the more familiar forms (reference 1, p. 24)

$$Q(1s \to 1s) = (4/k^2) \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l , \tag{IV.4}$$

and

$$I(1s \to 1s, \theta) = \left| \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta l} - 1) P_l(\cos\theta) \right|^2 \Big/ 4k^2 \tag{IV.5}$$

(b) Strong-Coupling Approximation

In this review, we shall give the name "strong coupling approximation" when any two s states, for example $1S$ and $2S$, of atomic hydrogen are taken in the eigenfunction expansions (III.41) and (III.42). The system of radial equations in (III.43) reduces to two coupled integro-differential equations (for electrons). For example, for $1S$-$2S$ coupling

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k_1^2\right] F_{10l}^{lS}(r) = \sum_{1s,2s} [V_{10,\nu'}^{l} - W_{10,\nu'}^{lS}] F_{\nu'}^{lS}(r)$$

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k_2^2\right] F_{20l}^{lS}(r) = \sum_{1s,2s} [V_{20,\nu'}^{l} - W_{20,\nu'}^{lS}] F_{\nu'}^{lS}(r) , \tag{IV.6}$$

which is called the *strong coupling exchange approximation.*

When the exchange terms of (IV.6) are neglected, we obtain the *strong coupling approximation* for either electrons (upper sign) or positrons (lower sign):

$$[d^2/dr^2 - l(l+1)/r^2 + k_1^2 \mp V_{1s,1s}] F_{10l}^{l}(r) = \pm V_{1s,2s} F_{20l}^{l}(r)$$

$$[d^2/dr^2 - l(l+1)/r^2 + k_2^2 \mp V_{2s,2s}] F_{20l}^{l}(r) = \pm V_{2s,1s} F_{10l}^{l}(r) \tag{IV.7}$$

In this approximation, it is possible to calculate four cross sections, namely, Q_{1s-1s}, Q_{1s-2s}, Q_{2s-1s}, and Q_{2s-2s}.

In the positron problem, if the two states to be coupled together are $1S$ atomic hydrogen and $1S$-positronium, then one must solve the following pair of coupled integro-differential equations:

$$\left[\frac{d^2}{dr_2^2} + k_1^2 - \frac{l(l+1)}{r_2^2} + V_{1s,1s}(r_2)\right] F^l(r_2) = \int_0^{\infty} K(r_2,R) G^l(R) dR$$

$$\left[\frac{d^2}{dR^2} + \kappa_1^2 - \frac{l(l+1)}{R^2}\right] G^l(R) = 2\int_0^{\infty} K(r_2,R) F^l(r_2) dr_2 \tag{IV.8}$$

TABLE III. Positron-hydrogen atom partial-wave phase shifts. Rows a, b, and c refer to the same approximations as those of Table I. Row d: static approximation, including the induced dipole-polarization potential; rows e and f present the results for coupling between 1s(H) and 1s(positronium) with and without polarization, respectively.

k^2 \ l		0	1	2
0.74	b	−0.3712	−0.0625	−0.0098
	c	−0.3414	−0.0234	0.0234
0.72	b	−0.3685	−0.0610	−0.0094
	c	−0.3867	−0.0300	0.0225
0.6972	a	−0.381	−0.063	−0.009
	b	−0.3673	−0.0594	−0.0089
	c	−0.3315	−0.0187	0.0220
0.64	a	−0.3713	−0.0584	−0.0082
	b	−0.3569	−0.0549	−0.0077
	c	−0.3223	−0.0143	0.0214
0.49	d	−0.1467		
	e	−0.2864		
0.36	a	−0.3043	−0.0322	−0.0028
	b	−0.2936	−0.0305	−0.0028
	c	−0.2461	0.0101	0.0183
	d	−0.0989		
	e	−0.2379		
	f	0.0950		
0.25	a	−0.264	−0.020	−0.0013
	b	−0.2547	−0.020	−0.0014
	c	−0.1990	0.0183	0.0152
	d	−0.0476		
	e	−0.186		
	f	0.1588		
0.16	a	−0.2181	−0.0121	−0.0005
	b	−0.2110	−0.0114	−0.0006
	c	−0.1472	0.0217	0.0112
	d	0.0048		
	e	−0.1339		
	f	0.2228		
0.09	a	−0.168	−0.0055	
	b	−0.163	−0.0053	−0.0003
	c	−0.0931	0.0201	0.0070
	d	0.0528		
	e	...		
	f	0.2754		
0.04	a	−0.1145	−0.0017	
	b	−0.1109	−0.0017	−0.0002
	c	−0.0426	0.0127	0.0031
	d	0.0853		
	e	−0.0465		
	f	0.2929		
0.01	a	−0.058		
	b	−0.0562		
	c	−0.0054	0.002	
	d	0.0803		
	e	...		
	f	0.2260		
0.0	a	0.582		
	b	0.564		
	c	...		
	d	−1.267		
	e	0.1704		
	f	−3.06		

Electrons: Bransden and McKee[53] have solved Eqs. (IV.7) for $l = 0$ and $k = 0.919$, 1.0, 1.2, 1.5,

---

[53] B. H. Bransden and J. S. C. McKee, Proc. Phys. Soc. (London) A67, 422 (1956).

TABLE IV. Electron-hydrogen atom partial wave excitation cross sections for $Q(1s\text{-}2s)$; the sum column includes an estimate of higher L contributions. The spin weighting factors of 3/4 (triplet) and 1/4 (singlet) have been included.

k^2	Spin State	Approximation	$L = 0$	$L = 1$	$L = 2$	$L = 3$	$L = 4$	$L = 5$	$L = 6$	Sum
0.81	Singlet	1*s*-2*s*	0.038	0.008	0.0					
		1*s*-2*s*-2*p*	0.0529	0.0045	0.0581	~0.003	0			0.119
	Triplet	1*s*-2*s*	0	0.1736	0.006					
		1*s*-2*s*-2*p*	0.0012	0.0709	0.0028	0.0175	0.002			0.094
1.0	Singlet	1*s*-2*s*	0.0714	0.051	0					
		1*s*-2*s*-2*p*	0.0766	0.0144	0.0822	0.0103	0.0018	0.0003		0.1858
	Triplet	1*s*-2*s*	0.0027	0.161	0.046	0.002				
		1*s*-2*s*-2*p*	0.0036	0.1219	0.0211	0.0208	0.0071	0.0012		0.1757
1.21	Singlet	1*s*-2*s*	0.070	0.0524	0.0003					
		1*s*-2*s*-2*p*	0.0588	0.0246	0.0645	0.0231	0.0054	0.0014		0.1779
	Triplet	1*s*-2*s*	0.0044	0.105	0.0262					
		1*s*-2*s*-2*p*	0.0051	0.1001	0.0316	0.0069	0.0113	0.0042		0.1592
1.44	Singlet	1*s*-2*s*	0.0547	0.053	0.0053					
		1*s*-2*s*-2*p*	0.0380	0.0256	0.0245	0.0247	0.0082	0.0028	0.0010	0.1255
	Triplet	1*s*-2*s*	0.0061	0.0735	0.0577					
		1*s*-2*s*-2*p*	0.0055	0.0716	0.0358	0.0036	0.0103	0.0065	0.0029	0.1380
2.25	Singlet	1*s*-2*s*	0.0238	0.0383	0.011					
		1*s*-2*s*-2*p*	0.0123	0.0309	0.0015	0.0040	0.0051	0.0037	0.0022	0.0624
	Triplet	1*s*-2*s*	0.0073	0.0358	0.040					
		1*s*-2*s*-2*p*	0.0045	0.0355	0.0302	0.0070	0.0045	0.0054	0.0046	0.0978
4.0	Singlet	1*s*-2*s*	0.0073	0.0157						
		1*s*-2*s*-2*p*	0.0049	0.0153	0.0068	0.0021	0.0010	0.0010	0.0010	0.0354
	Triplet	1*s*-2*s*	0.0046	0.0162		0.0143				
		1*s*-2*s*-2*p*	0.0030	0.0154	0.0175	0.0100	0.0045	0.0025	0.0021	0.0641

and 2.0; Smith *et al.*[45] have solved this system of equations for all significant partial waves and $k = 1.0$, 1.2, 1.5, and 2.0. It is emphasized that these calculations were carried out at energies *above* the excitation threshold. Smith and Burke[54] have calculated the elastic-scattering cross section for $k^2 < 0.75$ and $l = 0$, 1, and 2; the numerical methods required to take into account *virtual* excitations are somewhat more sophisticated than for real excitations. The results of these calculations represent only approximations to the more elaborate computations to be quoted here. Therefore, we do not reproduce the nonexchange results but refer the reader to the original papers. The most significant fact to emerge from these calculations was the indication that $l > 0$ partial waves are much more important than had been accepted previously.[45]

Marriott[55] was first to solve the coupled system of integro-differential equations given in (IV.6). He calculated the zero-order partial-wave cross sections ($l = 0$) for $k = 0.9$, 1.0, 1.1, 1.2, 1.5, and 2.0. Marriott's work, i.e., *above* excitation thresholds, was extended by Smith[56] to include all significant partial wave contributions to the cross sections. The partial-wave cross sections for $Q(1S\text{-}2S)$ are given in Table IV. Smith and Burke,[54] and Smith *et al.*[57] have performed extensive calculations for $l = 0$, 1, and 2 *below* excitation thresholds. The phase shifts are reproduced in Table II.

Positrons: Smith *et al.*[45] have solved Eq. (IV.7) for the same ranges of k and l that they used for the electron problems and the partial-wave cross sections are given in Table V. while Smith and Burke[54] have calculated the *s*, *p*, and *d* waves including virtual excitation to the $2S$ state. The phase shifts are given in Table III. The explicit form of the kernels in Eq. (IV.8) have been derived by Cody and Smith[58] and numerical solutions for $k^2 < 0.5$ (the threshold for positronium formation) have been obtained[59] and are quoted in Table III.

It should be pointed out that the *distorted-wave approximation* is derived from the above by setting the coupling terms in one of the pair of equations equal to zero; this approximation is the simplest [other than Born approximations, which will be discussed in Sec. VI(g)] for calculating excitation

---

[54] K. Smith and P. G. Burke, Phys. Rev. **123**, 174 (1961).

[55] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).

[56] K. Smith, Phys. Rev. **120**, 845 (1960).

[57] See reference 12a.

[58] W. J. Cody and K. Smith, Argonne National Laboratory Report, ANL-6121 (1960) (unpublished); see also W. J. Cody, Argonne National Laboratory Report, ANL/AMD-21 (1961) (unpublished).

[59] H. S. W. Massey, J. Lawson, W. J. Cody, and K. Smith (unpublished).

TABLE V. Positron-hydrogen atom partial-wave cross sections. Rows b and c have their usual meanings.

k^2	l	Q_{1s-1s}			Q_{1s-2s}			Q_{2s-2s}			Q_{1s-2p}		
		0	1	2	0	1	2	0	1	2	0	1	2
0.81	c	0.5855			0.0070			21.85			0.005		
1.0	b	0.6082	0.0760	0.0047	0.0093	0.0077	0.0015	15.04	13.17	3.21			
	c	0.5406			0.0070			0.56			0.011		
1.21	c	0.4957	0.0314		0.0091	0.0345		0.20	6.63		0.013	0.040	
1.44	b	0.4866	0.0898	0.0087	0.0192	0.0207	0.0074	5.71	9.01	5.00			
	c	0.4529	0.0427		0.0124	0.0403		0.76	4.20		0.012	0.048	
2.25	b	0.3563	0.0990	0.0155	0.0209	0.0282	0.0153	2.58	4.64	3.63			
	c	0.3434	0.0705		0.0171	0.0427		1.29	2.86		0.005	0.042	
4.0	b	0.2205	0.0935	0.0243	0.0125	0.0213	0.0170	1.11	1.95	1.80			
	c	0.2182	0.0849	0.0204	0.0116	0.0279	0.0279	0.87	1.62	1.51	0.001	0.020	0.050

cross sections. Ochkur[49] has used such an approximation to calculate a single partial-wave contribution to the excitation cross sections from the $1S$ state to the $2S$, $2P$, $3S$, $3P$, $3D$, $4S$, and $4D$ for $1.0 \leqslant k \leqslant 2.23$. Khashaba and Massey[60] have also used this approximation to calculate a partial-wave cross section for Q_{1s-2p} for $k = 1.0$, 1.2, 1.5, and 2.0.

The boundary conditions to be imposed on the solutions to the pair of equations in the strong coupling approximation depend on k_2^2. If $k_2^2 > 0$, then F_{1Sl}^l and F_{2Sl}^l, which we shall label F_n^l, $n = 1S$ or $2S$, must satisfy [see Eq. (III.8)]

$$F_n^l(0) = 0\,,$$

$$F_n^l(r) \backsim \delta_{nj} i^l (2l+1) \sin(kr - l\pi/2)/k + c_{nj}^l e^{ikr}\,, \qquad \text{(IV.9)}$$

where j represents the initial state of the system. The numerical solution of Eq. (IV.7–9) will have the asymptotic form $A_n \sin(k_n r - l\pi/2 + \delta_n^l)$. For a pair of coupled second-order ordinary differential equations it is necessary to obtain two linearly independent solutions. Let B_n^l and η_n^l be the parameters of the second solution. Then the total excitation cross section Q_{1s-2s} is given by[55]

$$Q(1s \to 2s) = \sum_{l=0}^{\infty} \frac{4k_2(2l+1)\sin^2(\delta_2^l - \eta_2^l)}{k_1^3[(A_1^l/A_2^l)^2 + (B_1^l/B_2^l)^2 - 2(A_1^l B_1^l/A_2^l B_2^l)\cos(\delta_1^l - \delta_2^l - \eta_1^l - \eta_2^l)]}\,. \qquad \text{(IV.10)}$$

The elastic-scattering cross section is given by

$$Q(1s \to 1s) = \frac{4}{k_1^2} \sum_{l=0}^{\infty} \frac{(2l+1)[A^2 \sin^2 \delta_1^l + \sin^2 \eta_1^l - 2A \sin \delta_1^l \sin \eta_1^l \cos(\delta_2^l - \eta_2^l)]}{A^2 + 1 - 2A\cos(\delta_2^l - \delta_1^l - \eta_2^l + \eta_1^l)}\,, \qquad \text{(IV.11)}$$

where

$$A \equiv A_1^l B_2^l / A_2^l B_1^l\,.$$

The explicit formulas (IV.10) and (IV.11) are reduced forms of Eq. (III.31).

The cross sections Q_{2s-2s} and Q_{2s-1s} are given by the same expressions as (IV.11) and (IV.10) with (k_1, δ_1, A_1, η_1, B_1) ↔ (k_2, δ_2, A_2, η_2, B_2). An IBM-704 code for calculating the various elastic and inelastic cross sections for any number of S states is given elsewhere.[61]

If $k_1^2 < 0.75$ (for electrons), then F_1^l is required to have the asymptotic form given in Eq. (IV.9), whereas F_2^l must be asymptotic to a decaying exponential,

$$F_2^l \backsim c_{21}^l \exp(-|k_2|r)\,, \qquad \text{(IV.12)}$$

since the incident projectile no longer has sufficient energy to excite the hydrogen atom. In this case, there will be only one real phase shift and the cross sections will be given by Eqs. (IV.4) and (IV.5).

It should be pointed out that the approximations considered so far in this section only involve S states in the eigenfunction expansion. As shown in Castillejo *et al.*,[27] these S states do *not* contribute to the polari-

---

[60] S. Khashaba and H. S. W. Massey, Proc. Phys. Soc. (London) **71**, 574 (1958).

[61] K. Smith, Argonne National Laboratory Report, ANL-6095 (1960) (unpublished).

zation potential, U_p. Hence, the above approximations cannot make any statement about the effect of atomic polarizability in scattering problems. In this connection see Sec. VI (a).

(c) Close-Coupling Approximation

In the previous section a description has been given of the work done using the strong-coupling approximation involving just S states in the eigenfunction expansion. This approximation suffers from two main defects. Firstly the dipole polarization potential U_p is completely neglected, and secondly, as has been noted by several workers,[62,63] in calculating excitation cross sections, it is important to include all degenerate eigenfunctions, in the initial and final states, in the expansion. We may thus, for example, expect the $2p$ state to play an important role in the calculation of the Q_{1s-2s} cross section. The neglect of the dipole polarization is expected to give results most in error for energies near thresholds and for the higher angular momenta. Near a threshold the wave function in the threshold channel is, in the asymptotic region, close to a straight line and, therefore, the long range effect of U_p is not canceled by oscillations in the wave function. For high angular momenta the centrifugal barrier causes only the asymptotic region in the wave function to be significant.

The obvious and most useful extension to the strong-coupling approximation is the inclusion of the $1s$, $2s$, and $2p$ eigenfunctions of hydrogen in the expansion. This will first allow a more accurate evaluation of Q_{1s-2s} and second will automatically include, by virtue of the $2p$ state, 65.77% of the correct hydrogen atom polarizability.[27] The values of ν required in Eq. (III.43) are obtained using the triangular inequality for (l_1l_2L). In Table VI we give the l_2 values for various l_1 and L.

The set of coupled equations corresponding to (IV.6) now become, in general, four in number for each spin and total angular momentum. As before, the $1s$ and $2s$ states each couple to the $l_2 = L$ component of the scattered electrons and give one equation each. The $2p$ state, however, gives two equations, being coupled to the $l_2 = L - 1$ and $l_2 = L + 1$ component of the scattered electron. When $L = 0$, the $l_2 = L - 1$ channel drops out and we are left with a set of three coupled equations. The term involving the $2p$ state coupled with the $l_2 = L$ component of the scattered electron has opposite parity to the above set of equations and therefore does not itself add to their number in the representation in which parity is diagonal. Instead it forms a single equation which need only be solved if Q_{2p-2p} is being calculated. We have, therefore, that in this approximation it is possible to calculate nine cross sections, namely, Q_{1s-1s}, Q_{1s-2s}, Q_{1s-2p}, Q_{2s-1s}, Q_{2s-2s}, Q_{2s-2p}, Q_{2p-1s}, Q_{2p-2s}, and Q_{2p-2p}.

TABLE VI. l_2 values in the electron- (or positron-) hydrogen atom problem in the Γ representation, where parity $(-1)^{l_1+l_2} = (-1)^L$.

L \ n,l_1	1,0	2,0	2,1	3,0	3,1	3,2
0	0	0	1	0	1	2
1	1	1	0 2	1	0 2	1 3
2	2	2	1 3	2	1 3	0 2 4
3	3	3	2 4	3	2 4	1 3 5

In the positron problem the same approximation is valid provided the exchange potentials are dropped and the direct potentials have their sign changed. Of course, in order to include real or virtual positronium formation, eigenstates of positronium must be added to the expansion which couples in extra equations.[38]

Electrons: Burke and Schey[64] have solved the $1s$, $2s$, and $2p$ approximation equations for $L = 0$, 1, 2 and 3 and for a series of energies less than the second quantum excitation threshold. Their phase shifts are presented in Table II. They also solved, for the $L = 0$ singlet state and for $k^2 = 0.55$ and 0.60, the coupled equations resulting from the inclusion of the $3s$, $3p$, or $3d$ states as well as the $1s$, $2s$, and $2p$ in the eigenfunction expansion. This was in order to gain information on the convergence of the hydrogen eigen-

TABLE VII. Electron-hydrogen atom $L = 0$ (singlet) partial-wave phase shifts in the close-coupling approximation including various hydrogen atom eigenstates.

States Included	$k^2 = 0.55$	$k^2 = 0.60$
$1S$	0.7004	0.6704
$1S$-$2S$	0.7352	0.7115
$1S$-$2p$	0.7352	0.7040
$1S$-$2S$-$2p$	0.7846	0.7707
$1S$-$2S$-$2p$-$3S$	0.7894	0.7738
$1S$-$2S$-$2p$-$3p$	0.7920	0.7770
$1S$-$2S$-$2p$-$3d$	0.7841	0.7694
$1S$-$2S$-$2p$-$3S$-$3p$	0.7975	0.7814
Schwartz[a]	0.908	0.894

[a] See reference 93.

---

[62] D. G. Hummer and M. J. Seaton, Phys. Rev. Letters 6, 471 (1961).

[63] N. A. Kroll and E. Gerjuoy, *Second International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), 23.

[64] See reference 12b.

function expansion. These phase shifts are presented in Table VII.

Above the $N = 2$ threshold, preliminary work by Burke, Burke, McCarroll, and Percival[65] including the $1S$, $2S$, and $2p$ states has been extended by Burke, Schey, and Smith[66] to include all significant partial waves for $k = 0.9$, 1.0, 1.1, 1.2, 2.5, and 2.0. Cross sections for $Q(1s\text{-}2s)$ and $Q(1s\text{-}2p)$ are given in Tables IV and VIII, respectively.

TABLE VIII. Electron-hydrogen atom partial wave excitation cross sections: row a $Q(1s\text{-}2p)$, in the close-coupling approximation $1s\text{-}2s\text{-}2p$; row b $Q(1s\text{-}3p)$ in the strong-coupling approximation $1s\text{-}3p$. Contributions from $L > 5$ are included in the sum.

k^2			$L = 0$	$L = 1$	$L = 2$	$L = 3$	$L = 4$	$L = 5$	Sum
0.81	Singlet	a	0.038	0.075	0.109				0.2334
	Triplet	a	0.00	0.07	0.007	0.051			0.1265
1.00	Singlet	a	0.036	0.110	0.2530	0.0353	0.0098	0.0025	0.4481
		b	0.0036	0.0152					
	Triplet	a	0.00	0.080	0.0458	0.1671	0.0438	0.0093	0.3518
		b	0.0	0.044					
1.21	Singlet	a	0.036	0.1105	0.340	0.0863	0.030	0.0112	0.6212
		b	0.0059	0.0086					
	Triplet	a	0.007	0.063	0.0548	0.1831	0.1046	0.038	0.4727
		b	0.0004	0.0208					
1.44	Singlet	a	0.034	0.081	0.2895	0.1256	0.0508	0.023	0.6243
		b	0.0025	0.0074	0.0773				
	Triplet	a	0.009	0.042	0.0537	0.1740	0.1404	0.073	0.5558
		b	0.0007	0.0104	0.0014				
2.25	Singlet	a	0.0171	0.0176	0.0942	0.0999	0.0695	0.045	0.4275
		b	0.0004	0.0031	0.0191	0.0240			
	Triplet	a	0.0106	0.0133	0.0357	0.1076	0.1342	0.115	0.6636
		b	0.0008	0.0016	0.0024	0.0186			
4.0	Singlet	a	0.0035	0.0024	0.0169	0.0302	0.0347	0.0329	0.2640
		b	0.0	0.0006	0.0033	0.0065	0.0078		
	Triplet	a	0.0052	0.0038	0.0139	0.0394	0.0624	0.0728	0.6076
		b	0.0003	0.0002	0.0015	0.0068	0.0126	0.0156	

Positrons: Burke *et al.*[66] have solved the $1S\text{-}2S\text{-}2P$ equations neglecting positronium formation for all significant partial waves and for a series of energies below and above the second quantum excitation energy. Their phase shifts and cross sections are given in Tables III and V, respectively.

The only significant numerical change from the methods used by Smith and Burke[54] in the $1S\text{-}2S$ strong coupling approximation is that made necessary by the long range of the dipole interaction. A more involved asymptotic expansion must be used to obtain the phase shift or $\mathcal{R}$-matrix elements in terms of the asymptotic form of the solution of the coupled equations. Details of this asymptotic expansion are given in the next section.

(d) Numerical Methods

In this section we shall describe the numerical methods that we have used to solve the systems of equations derived in the preceding sections. Different methods have been developed by other authors to solve particular cases of the problems which are posed here for numerical solution. In particular, we refer the reader to the integral equation method of Fraser,[67] the algebraic noniterative method of Percival,[55] the matrix method of Robertson[68] for a single integro-differential equation and of Pennell and Delves[69] for two coupled equations and the method proposed by Drukharev.[70]

We shall begin by sketching the problems to be considered, in order of increasing difficulty. The simplest problem is posed when we neglect either electron exchange, or positronium formation, and atomic distortion. That is, we are interested in the solution of a single equation of the type (IV.2), satisfying the boundary conditions (IV.9). A numerical method for solving such an equation is described.

The method is extended to treat the solution of the set of coupled second-order ordinary differential equations that arise when spherical distortion of the atomic electron charge cloud is allowed for by the inclusion of a small number of hydrogen S states in the eigenfunction expansion. In this latter problem, there can be one or more open channels satisfying the propagating asymptotic boundary conditions (IV.9), whereas the remaining channels are closed and are characterized by the decaying asymptotic boundary conditions (IV.12). The exact number in each category depends on the number and type of states included in the original expansion, and also on the incident energy. The presence of the closed channels requires special numerical consideration.

The inclusion of either electron exchange or positronium formation introduces integral terms into the differential equations and we present numerical methods that have been developed to deal with these terms.

Finally, nonspherical atomic distortion is allowed

---

[65] P. G. Burke, V. M. Burke, R. McCarroll, and I. C. Percival, Proc. Phys. Soc. (London) (to be published); V. M. Burke and R. McCarroll, *ibid.* (to be published).

[66] P. G. Burke, H. M. Schey, and K. Smith (unpublished); this problem is also being solved by Omidvar and by Danburg and Peterkop.

[67] P. A. Fraser, Scientific Report, No. 4, Department of Physics, University of Western Ontario, London, Ontario, Canada; see McEachran's extension of this method in reference 57.

[68] H. H. Robertson, Proc. Cambridge Phil. Soc. **52**, 538 (1956).

[69] M. M. Pennell and L. M. Delves, Math. Comp. **15**, 243 (1961).

[70] G. F. Drukharev, J. Exp. Theoret. Phys. U.S.S.R. **19**, 247 (1949).

for by including nonspherical hydrogen states in the eigenfunction expansion. This entails a more sophisticated treatment of the asymptotic boundary conditions, owing to the presence of long range interactions. The modifications required here will be briefly reviewed.

The solution of a single second-order ordinary differential equation of the type (IV.2) is completely specified by two constants. One of these constants is used to satisfy the physical requirement that we take the solution which is regular at the origin. The other provides an over-all normalization, which, of course, does not affect the phase shift and cross section. Therefore, we can expand the solution of (IV.2) about the origin as follows:

$$F^l(r) = r^{l+1}\sum_{i=0}^{\infty} a_i^l r^i\,, \qquad \text{(IV.13)}$$

where a_0^l is the arbitrary normalization constant and a_i^l, for $i \geqslant 1$, can be obtained in terms of a_0^l by substituting (IV.13) into (IV.2) and equating the coefficients of successive powers of r. If we are given $F^l(r_0)$, $F^l(r_0)'$, and $F^l(r_0)''$ as starting values at some value of $r = r_0$, then the differential equation can be numerically integrated step by step using standard techniques (for example, the Runge-Kutta method, see Gill[71]). For equations of the type (IV.2), the numerical integration is started at some small r_0 and continued out to a region where the potential term is negligible.

For $l = 0$ and 1, r_0 can be taken to be zero since $F^l(0)$, $F^l(0)'$, and $F^l(0)''$ uniquely define the solution. For $l \geqslant 2$, however, these three quantities are all zero and it is necessary to give r_0 some small nonzero value and to determine the relation between $F^l(r_0)$, $F^l(r_0)'$, and $F^l(r_0)''$ using Eq. (IV.13).

In the asymptotic region, where the potential is effectively zero, we can *fit* our numerical solution to the analytic form [see Eqs. (III.23) and (III.47)].

$$F^l(r) = a[krj_l(kr) - \tan\delta_l(krn_l(kr))] \backsim A^l \sin(kr - \tfrac{1}{2}l\pi + \delta_l)\,. \qquad \text{(IV.14)}$$

This fit is effected by using either the value of the function and its derivative at one point, or the function at two points. Thus, the phase shift δ_l and the asymptotic normalization constant a can be determined. At zero energy, the solution is fitted to the analytic form (III.48) and the scattering length A^L evaluated.

For n coupled second-order ordinary differential equations it is necessary to specify $2n$ constants in some way before the numerical solution can be obtained. At the origin, n of these constants are determined by requiring all the functions F_i^l $(1 \leqslant i \leqslant n)$ to be regular. Of the remaining n constants, n_b are fixed, since the logarithmic derivative $F_i^l(r)'/F_i^l(r)$ in the n_b closed channels is asymptotically equal to $(-k_i)$. The remaining n_a constants, corresponding to the n_a open channels $(n_a + n_b = n)$, allow n_a linearly independent solutions of the differential equations to be evaluated. In each of the n_a open channels, the functions automatically satisfy the asymptotic boundary conditions (IV.9). The n_a linearly independent solutions allow all the elements of the A and B matrices, Eq. (III.16), to be evaluated and consequently the $\mathcal{R}$ matrix and cross sections to be determined.[61]

As in the case of a single equation, each function can be expanded in the form (IV.13) about the origin, and it is thus possible to define n linearly independent solutions satisfying the boundary conditions at the origin. For an incident electron energy less than that required to excite all the states included in the eigenfunction expansion, the numerical solutions obtained in the outward integration will contain some of the positive exponential solution in the closed channels. This solution will dominate the required decaying exponential more and more as r increases. In order to avoid the appearance of the $\exp(|k_i|r)$ term, the asymptotic conditions are imposed at the outset. That is, the outward solution of the system of equations is stopped at some point r_0, say, which is not in the asymptotic region. The numerical solution is restarted in the asymptotic region, imposing the boundary conditions (IV.12) for all n_b closed channels, and a backward, or *inward* numerical integration to r_0 is performed.

Since $n + n_a$ constants can be specified arbitrarily in the asymptotic region, it is necessary to extract $n + n_a$ linearly independent solutions in the outer region. The n outward solutions and the $n + n_a$ inward solutions, and their first derivatives, are matched at r_0 by requiring the continuity of $F_i^l(r)$ and $F_i^l(r)'$. The matching condition is[54]

$$\sum_{\alpha=1}^{n} u_\alpha \begin{pmatrix} F_i^l(r_0) \\ F_i^l(r_0)' \end{pmatrix}_\alpha = \sum_{\beta=1}^{n+n_a} w_\beta \begin{pmatrix} F_i^l(r_0) \\ F_i^l(r_0)' \end{pmatrix}_\beta\,, \qquad \text{(IV.15)}$$

where u_α and w_β are $2n + n_a$ arbitrary coefficients to be determined from these $2n$ equations. The n_a degrees of freedom are used to impose n_a integral conditions as the n_a open channel functions. These integral conditions are taken (quite arbitrarily) to be

$$\sum_{\alpha=1}^{n} u_\alpha \int_0^{r_0} {}_\alpha F_i^l(r)dr + \sum_{\beta=1}^{n+n_a} w_\beta \int_{r_0}^{r_m} {}_\beta F_i^l(r)dr = C_i\,, \qquad \text{(IV.16)}$$

---

[71] S. Gill, Proc. Cambridge Phil. Soc. 48, 96 (1951).

where r_m can be chosen arbitrarily, usually within the first loop of F_1.

The real coefficients C_i ($i = 1 \rightarrow n_a$) can be chosen arbitrarily. Each linearly independent vector C_i generates a linearly independent solution, $F_i(r)$. Thus the complete set of solutions to the differential equations satisfying the boundary conditions (IV.9) and (IV.12) are obtained by using any set of n_a linearly independent vectors C_i which span the appropriate n_a-dimensional space. We may take, as a linearly independent choice of the vectors C_i, the set

$$C_1 = \begin{pmatrix} +1 \\ +1 \\ +1 \\ \vdots \\ +1 \end{pmatrix} \quad C_2 = \begin{pmatrix} +1 \\ -1 \\ +1 \\ \vdots \\ +1 \end{pmatrix}, \cdots, C_{n_a} = \begin{pmatrix} +1 \\ \vdots \\ +1 \\ +1 \\ -1 \end{pmatrix}. \tag{IV.17}$$

It should be noted that when all n channels are open, e.g., when just the $1S$ and $2S$ hydrogen states are coupled and $k_1^2 > 0.75$, it is not necessary to use such an elaborate procedure as implied by Eqs. (IV.15) and (IV.16). It is then possible, owing to the stability of the solution, to carry the *forward* integration from the origin into the asymptotic region, as in the case of the solution of a single equation. The required n linearly independent solutions are then obtained by imposing n linearly independent boundary conditions, consistent with (IV.13), at the origin, and the $\mathcal{R}$ matrix and cross section are obtained by matching the solutions in the asymptotic region to boundary conditions of the form (IV.14). This was the method used in reference 45.

When either electron exchange or positronium formation is taken into account, then systems of integro-differential equations, of the type (IV.1), (IV.6), and (IV.8), must be solved. If all the channels are open then a straightforward iterative technique can be used. In the first iteration, the integral terms are neglected and a first approximation to the asymptotic parameters ${}^1A_i^l$ and ${}^1\delta_i^l$, is obtained for the function ${}^1F_i^l$. This approximation to the function, ${}^1F_i^l$, is used in the integral terms and the resulting system of inhomogeneous differential equations is solved using the same starting conditions as in the first iteration. A second estimate to the true asymptotic parameters is obtained: ${}^2A_i^l$ and ${}^2\delta_i^l$. The iterative scheme is continued until the asymptotic parameters in successive iterations differ to within a specified epsilon. This procedure is repeated for each of the n linearly independent solutions which are required.[56]

When some of the channels are closed the above iteration procedure must be modified. In the first iteration a matched solution is obtained as described above, using the conditions (IV.15) and (IV.16). This matched solution is substituted into the integral terms and the resulting system of inhomogeneous equations is solved once in the inner region, $r \leqslant r_0$, and once in the outer region, $r \geqslant r_0$. The matching condition is now

$$\begin{pmatrix} \mathfrak{F}_i^l(r_0) \\ \mathfrak{F}_i^l(r_0)' \end{pmatrix}_{\text{in}} + \sum_{\alpha=1}^{n} u_\alpha \begin{pmatrix} F_i^l(r_0) \\ F_i^l(r_0)' \end{pmatrix}_\alpha = \begin{pmatrix} \mathfrak{F}_i^l(r_0) \\ \mathfrak{F}_i^l(r_0)' \end{pmatrix}_{\text{out}} + \sum_{\beta=1}^{n+n_a} w_\beta \begin{pmatrix} F_i^l(r_0) \\ F_i^l(r_0)' \end{pmatrix}_\beta \tag{IV.18}$$

and the integral conditions for $i = 1 \rightarrow n_a$ are

$$\int_0^{r_0} \left\{ \mathfrak{F}_i^l(r)_{\text{in}} + \sum_{\alpha+1}^{n} u_\alpha F_i^l(r)_\alpha \right\} dr + \int_{r_0}^{r_m} \left\{ \mathfrak{F}_i^l(r)_{\text{out}} + \sum_{\beta+1}^{n+n_a} w_\beta F_i^l(r)_\beta \right\} dr = C_i \,, \tag{IV.19}$$

where $\mathfrak{F}$ are the particular solutions to the inhomogeneous equations. Our new continuous solution is then the sum of the particular solution plus that linear combination of the complementary functions given by the solution of (IV.18) and (IV.19). This new matched solution is substituted into the integral terms and the iteration process continued until the required degree of convergence is attained.

In certain circumstances, convergence by the above methods may be extremely slow or even nonexistent. For instance, the iterates may oscillate about some sort of average solution and the amplitude of the oscillation decrease only slowly or even increase. Even worse, the solution may monatonically diverge away from the correct solution and no starting value will give convergence. These difficult circumstances are exceptional for reasonable choices or r_m, which is usually taken to lie within the first loop of the propagating functions [in order to avoid cancellation in the integrals (IV.16) and (IV.19)]. However, they do occasionally occur.

One quite powerful technique which often gives convergence in these cases is to replace the p_{th} iterate, ${}^pF$, by a linear combination of the p_{th} and $(p-1)_{\text{th}}$ iterates, $\lambda\, {}^pF + (1-\lambda)\, {}^{p-1}F$, where λ can assume any predetermined real value. This new function is then used to evaluate the integral terms and the iteration process continued. The standard method described above corresponds to taking $\lambda = 1$. Giving λ some value between 0 and 1 is usually sufficient to avoid the oscillatory difficulty. Taking $\lambda < 0$ helps to avoid the monatonically diverging iterations, while taking $\lambda > 1$ tends to speed slow monotonically converging iterations. The choice of λ may be made, for instance, by looking at the asymptotic form of the iterates and may of course be varied from iteration to iteration.

Another method for obtaining rapid convergence has been used with success by Saraph and Seaton[72] in the case of a single integro-differential equation. If ${}^{\circ}F$ is the zero-order solution and ${}^{p}F$ is the p_{th} iterate a new solution is defined by ${}^{p}F' = {}^{p}F + a\, {}^{\circ}F$. The constant a is determined by substituting ${}^{p}F'$ into the Kohn variational principle (III.39) and allowing a to vary. The new function obtained in this manner is used as the basis for the next iteration and the process continued until convergence is obtained. The method can obviously be extended to treat n coupled integro-differential equation. The n_a equations (IV.19) are replaced by n_a equations obtained by adding onto some continuous solution, defined by (IV.18), arbitrary amounts of the n_a linearly independent homogeneous solutions obtained using (IV.15) and (IV.16). This new function is substituted into the Kohn variational principle and the n_a parameters determined. It is important that the continuous solution, defined by (IV.18) at each step of the iteration, should be selected so that it obeys the same boundary conditions, in some sense, as the previous Kohn-determined iterate. This can be achieved, for instance, by using (IV.19) as a subsidiary condition in defining the continuous solution. The C_i, however, are now modified from iteration to iteration and are chosen to have the value given by the previous Kohn-determined iterate.

A further difficulty sometimes appears in the solution of the integro-differential equations occurring in the electron case. This arises from the nonuniqueness of the solution. For example, it was found in the numerical solution of Eq. (IV.6), in the triplet state for $k^2 < 0.75$, that the s-partial wave phase shift, δ_0, did not vary smoothly with energy. An extra π or two appeared occasionally. This effect had been observed previously by Swan,[73] who explained it as being caused by the appearance of k-independent components in the solution of the integro-differential equations. In the triplet state, the spatial wave function can be written as

$$\Psi(r,r') = [\psi_1(r')\psi_2(r')] \begin{pmatrix} F_1(r)/r \\ F_2(r)/r \end{pmatrix} - [\psi_1(r)\psi_2(r)] \begin{pmatrix} F_1(r')/r' \\ F_2(r')/r' \end{pmatrix} . \tag{IV.20}$$

The numerical solution can be written in the form

$$\begin{pmatrix} F_1(k_1r)/r \\ F_2(k_2r)/r \end{pmatrix} = \begin{pmatrix} \mathcal{F}_1(k_1r)/r \\ \mathcal{F}_2(k_2r)/r \end{pmatrix} + a \begin{pmatrix} \psi_1(r) \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ \psi_2(r) \end{pmatrix} + c \begin{pmatrix} \psi_2(r) \\ \psi_1(r) \end{pmatrix} , \tag{IV.21}$$

where the last three terms on the right-hand side are k independent and satisfy the equation $\Psi = 0$. Hence $\Psi(F) \equiv \Psi(\mathcal{F})$, where the functions $\mathcal{F}$ do not contain any hydrogen atom contributions. The arbitrary constants a, b, and c can be chosen so as to make $\mathcal{F}_1/r$ orthogonal to ψ_1 and ψ_2 and $\mathcal{F}_2/r$ orthogonal to ψ_2. That is,

$$a \equiv \int_0^\infty r\psi_1 F_1 dr, \quad b \equiv \int_0^\infty r\psi_2 F_2 dr \text{ and } c \equiv \int_0^\infty r\psi_2 F_1 dr . \tag{IV.22}$$

The triplet phase shifts calculated from this "orthogonalized" vector $\mathcal{F}$ did indeed vary smoothly with energy. These are the values presented in the tables.

A similar situation can occur in the singlet state. Here the spatial wave function can be written

$$\Psi(r,r') = [\psi_1(r')\psi_2(r')] \begin{pmatrix} F_1(r)/r \\ F_2(r)/r \end{pmatrix} + [\psi_1(r)\psi_2(r)] \begin{pmatrix} F_1(r')/r' \\ F_2(r')/r' \end{pmatrix} \tag{IV.23}$$

and the numerical solution has the form

$$\begin{pmatrix} F_1(k_1r)/r \\ F_2(k_2r)/r \end{pmatrix} = \begin{pmatrix} \mathcal{F}_1(k_1r)/r \\ \mathcal{F}_2(k_2r)/r \end{pmatrix} + a \begin{pmatrix} \psi_2(r) \\ -\psi_1(r) \end{pmatrix} , \tag{IV.24}$$

where a can be chosen so that $\mathcal{F}_2/r$ is orthogonal to ψ_1.

In general, if n terms are retained in the close-coupling approximation, then $n(n+1)/2$ such orthogonality conditions can be imposed in the triplet state and $n(n-1)/2$ conditions imposed in the singlet state. It is convenient to use these conditions to orthogonalize each F_n/r to all ψ_m, where $m \leqslant n$ in the triplet state and $m < n$ in the singlet state. We assume that the atomic states have been ordered according to increasing principal quantum number. The ordering of states within each principal quantum-number level is left arbitrary. The orthogonalized wave function is now unique and has a well-defined phase shift although, of course, owing to the finite range of the k-independent solution, the cross section is not altered by this orthogonalization process. The orthogonalization, as defined above, now implies that the range of the exchange potential in each channel

---

[72] M. J. Seaton (private communication).

[73] P. Swan, Proc. Roy. Soc. (London) A228, 10 (1955).

does not exceed the range of the atomic wave function in that channel. This corresponds to the physical requirement that exchange cannot occur until the incident electron penetrates the atomic cloud. The problem of the definition of the phase shift in the elastic scattering of a particle by a compound system has been investigated in detail by Temkin[74] and Rosenberg and Spruch.[75]

The orthogonality that can be imposed in the triplet state between F_1/r and ψ_1 has been used by Seaton[76] and John[46] in speeding the convergence of the solution of a single integro-differential equation. The arbitrary amount of k-independent solution which can exist at any stage of the iteration can, in some cases, numerically overwhelm the required solution in the region of small r. Thus, even if convergence is obtained the phase shift may be inaccurate. The orthogonality condition imposed after each iteration removes this difficulty.

Finally, we come to the modified treatment of the asymptotic region required when nonspherical hydrogen states are included in the eigenfunction expansion. The potential interaction then contains terms which behave asymptotically as inverse powers of r. In a region where the exchange terms are negligible the coupled equations can be written

$$d^2F_i/dr^2 = \textstyle\sum_{j=1}^{n} V_{ij}(r)F_j(r) \quad i,j = 1,\cdots,n\,. \tag{IV.25}$$

Here V_{ij} includes the direct potential, the centrifugal barrier and the energy terms as follows:

$$V_{ij}(r) = \sum_{\lambda=1}^{m_{ij}} \frac{a_{ij}^{\lambda}}{r^{\lambda+1}} + \frac{l_i(l_i+1)}{r^2}\,\delta_{ij} - k_i^2\delta_{ij}\,. \tag{IV.26}$$

In Eq. (IV.26) we use the fact that each element of the direct potential can be written as a finite sum of inverse powers or r, starting with a power no higher than -2. Thus, for example, the direct potential coupling of the $1s$ and $2p$ states of hydrogen is asymptotic to r^{-2}.

The solution of (IV.25) is now no longer expressible in terms of the usual spherical Bessel functions but must be written generally as

$$F_i(r) = \sum_{p=0}^{\infty} \left\{ \sum_{\kappa=1}^{m_a} [\sin(k_\kappa r)\alpha_p^{i\kappa} r^{-p} + \cos(k_\kappa r)\beta_p^{i\kappa} r^{-p}] + \sum_{\tau=1}^{m_b} \exp(-|k_\tau|r)\gamma_p^{i\tau} r^{-p} \right\}. \tag{IV.27}$$

We assume in (IV.27) that there are m_a different wave numbers k_κ, $\kappa = 1$ to m_a, above threshold, and m_b different wave numbers $|k_\tau|$, $\tau = 1$ to m_b, below threshold.

Substituting (IV.26) and (IV.27) into Eq. (IV.25) and equating the coefficients of the powers of $\sin(k_\kappa r)\, r^{-p}$, $\cos(k_\kappa r)\, r^{-p}$, and $\exp(-|k_\tau|r)\, r^{-p}$, for all relevant κ, τ, p, and i, recursion relations for the α, β, and γ can be derived. These relations are given explicitly in Burke and Schey.[64] A particular solution of (IV.25) satisfying these relations is uniquely specified by the $(n + n_a)$ parameters

$$\begin{aligned} &\alpha_0^{i\kappa(i)}, \quad \beta_0^{i\kappa(i)} && \text{where } i = 1 \text{ to } n_a \\ &\gamma^{i\tau(i)} && \text{where } i = n_a + 1 \text{ to } n\,, \end{aligned} \tag{IV.28}$$

where we mean by the notation $\kappa(i)$ [or $\tau(i)$], that κ (or τ) which is determined by the channel i. These $(n + n_a)$ parameters are used to define $(n + n_a)$ linearly independent solutions in the outside region. These, when combined with the solutions in the inner region, as described previously, give n_a linearly independent continuous solutions. The $\mathcal{R}$ matrix is related in the usual manner to the coefficients of the sine and cosine terms in the asymptotic expansion. That is, the $\mathcal{R}$ matrix is given in terms of the $2n_a^2$ parameters $\alpha_0^{i\kappa(i)}$, $\beta_0^{i\kappa(i)}$ for the n_a linearly independent solutions.

V. VARIATIONAL METHODS

(a) Principles

In the preceding section we have seen that current applications of the eigenfunction expansion approach are based on a variational principle, see Eq. (III.39). In that section, the trial functions were restricted to a special class of functions constructed from products of *known* functions (the atomic eigenfunctions) and functions which are solutions of certain one-dimensional second-order differential equations. However, no estimate of the error in the approximate wave function so constructed was attempted in Sec. IV.!

In the present section, we shall discuss those methods that do not assume, necessarily, "separable" trial functions. That is, some correlation between the projectile and atomic electron is included in the trial function. Until recently, no mathematical criterion was known for deciding whether the "separable" results were better or worse than the "correlation" results. That is, it was believed[36] that scattering phases calculated by variational methods were, in general, neither an upper nor a lower bound to the correct value. This fact caused a great deal of confusion, since it was not certain that the method im-

---

[74] A. Temkin, J. Math. Phys. **2**, 336 (1961).

[75] L. Rosenberg and L. Spruch, Phys. Rev. **121**, 1720 (1961).

[76] M. J. Seaton, Proc. Roy. Soc. (London) **A218**, 400 (1953).

proved when the number of variational parameters was increased.

Fortunately, some progress is currently being made on the problem of obtaining rigorous bounds on the error incurred in variational calculations due to the pioneering work of Kato[77] and the subsequent developments of Spruch and his collaborators. In this review, we shall attempt to summarize the principal results on the construction of minimum and maximum principles (rather than mere stationary principles), particularly those relevant to the scattering of electrons and positrons by hydrogen atoms. Such extremum principles substantially increase the usefulness of variational methods in scattering problems, since one merely compares the bounds obtained from the different approximations. Thus, ignoring the necessity for understanding which physical phenomena should be allowed for, one simply introduces a large number of parameters into the calculation and varies them until the best bound is found. This is a standard technique for the Schrödinger eigenvalue problem.[78]

Equation (III.39) provides the basis of a variational principle which will allow any elastic or reaction cross section to be calculated. Suppose we assume for F some trial analytic form F_t, which contains N adjustable parameters $p_1, p_2, \cdots p_N$. We can calculate a value I_t for I using F_t rather than the unknown true value. An approximation to $\mathcal{R}$, and therefore to the cross sections, can be obtained using the stationary property (III.39); this allows us to take

$$\partial I/\partial p_r = 0\,, \quad r = 1,2,\cdots N\,,$$
$$\partial I/\partial \mathcal{R} = C^2/2k\,, \tag{V.1}$$

giving $N+1$ equations from which p_r and $\mathcal{R}$ may be determined. Let this value of the element of the derivative matrix be $\mathcal{R}(t)$. A correction to this value is given by Eq. (III.40) to be

$$\mathcal{R}_{\nu\nu'}^{LS}(K) = \mathcal{R}_{\nu\nu'}^{LS}(t) - 2kI_t/C^2\,. \tag{V.2}$$

These equations form the basis of the Kohn[37] variational method, which gives $\mathcal{R}(k)$ correct to second order in the error in the wave functions.

A slightly different method has been suggested by Hulthen,[36] who demands that the trial functions satisfy the condition $I_t = 0$.

The problem of estimating the error incurred in variational calculations lies in estimating the residual term

$$\iint \delta\Psi(H-E)\delta\Psi dr_1 dr_2$$

of Eq. (III.38). In the following paragraphs, we shall outline the steps by which progress has been made on this problem.

Kato[77] took the initial step in solving the problem of estimating the error incurred in the application of variational methods to collision problems. Kato developed a method for estimating upper and lower bounds on the elements of the $\mathcal{R}$ matrix in variational methods applied to *one-dimensional* problems. (We recall that the electron-hydrogen atom problem can be reduced to three independent variables, for example r_1, r_2, and $\hat{r}_1\cdot\hat{r}_2 \equiv p$ in Hylleraas[79] coordinates.) Spruch and Rosenberg[80] have also considered the one-dimensional problem. They have shown that for $k=0$, and for static potentials not attractive enough to form bound states of the overall system, both the Kohn and Hulthen variational principles provide upper bounds on the scattering length.[39]

Spruch and Rosenberg[81,82] generalized Kato's result to apply to scattering by a compound system, for example, the hydrogen atom. For $k=0$, and no composite bound state of the projectile plus target system, they were able to show that the Kohn variational principle provides an upper bound on the scattering length. For $k>0$, they were not able to obtain a bound on the phase shift. However, when they replaced the true problem by a fictitious problem, with cutoff potentials, they were able to obtain an upper bound on η.

The extension of the preceding result for $k=0$, to the case where one or more composite bound states do exist for the scattering of one compound system by another, has been carried out by Rosenberg, Spruch, and O'Malley.[83,84] Ohmura[85] has also shown that Hulthén's method guarantees the minimum nature of the scattering length in the e^-H problem. However, in the singlet state, the trial function must be constructed orthogonal to the bound state wave functions.

---

[77] T. Kato, Progr. Theoret, Phys. (Kyoto) **6**, 394 (1951). For the $L > 0$ partial waves, see L. Spruch and M. Kelly, Phys. Rev. **109**, 2144 (1958).

[78] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[79] E. A. Hyllerass, Z. Physik, **54**, 347 (1929); see also P. M. Morse and Feshback, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York), p. 1725 (1953). For $L > 0$, the Schrödinger equation reduces to sets of three-dimensional coupled partial differential equations.

[80] L. Spruch and L. Rosenberg, Phys. Rev. **116**, 1034 (1959).

[81] L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960).

[82] L. Spruch and L. Rosenberg, Phys. Rev. **117**, 1095 (1960).

[83] L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **118**, 184 (1960).

[84] L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **119**, 164 (1960).

[85] T. Ohmura, J. Math. Phys. **1**, 27 (1960).

TABLE IX. Summary of the present status of theoretical work in developing extrema principles for single-channel processes.

k	Problem	Composite Bound State	Bound	Restriction	Reference
>0	one-dimension	no	upper and lower on cot η		77
0	one-dimension	no	upper on A		80
0	e^+-H	no	upper on A		81
>0	e^+-H	no	upper on η	cutoff $V(r)$	
0	n-d	no	upper on A		82
0	e^--H (singlet)	yes	upper on A		83
0	e^--H (singlet, triplet)	yes	upper on A		84
>0	one dimension	yes	upper on $-1/(k \cot \eta)$; upper and lower on η.	cutoff $V(r)$	86
>0	e^--H (triplet)	yes	upper on $-1/(k \cot \eta)$	cutoff $V(r)$	75

Rosenberg and Spruch[86] extended the above results to $k > 0$ for the one-dimensional problem, taking into account bound states. They were able to give an upper bound to $-1/k \cot \eta$ for the problem with cutoff potentials. An upper bound on $-1/k \cot \eta$ in the scattering of one compound system by another, again with cut off potentials, has been given by the same authors.[75]

All of these results can be seen at a glance by looking at Table IX. Basically, the method simply consists of expressing the scattering length as a variational estimate plus an error term which is of second order in the error in the wave function, and then calculating a bound on the error term.

(b) Bounds on the Elements of the $\mathcal{R}$ Matrix

In this section, we shall be concerned mainly with incident energies too low for excitation of the target hydrogen atom, $k^2 < 0.75$, and too low for positronium formation, $k^2 < 0.5$. At these low energies only elastic scattering can occur, i.e., a single channel process. Before going on to discuss those results relevant to physical problems of interest here, we shall outline Kato's basic ideas in the one-dimensional problem.[77]

The starting point in Kato's paper is the one-dimensional analog to Eq. (III.38). That is, for the $l = 0$ partial wave, the derivative matrix is given by ($C^2 \equiv 1$)

$$\mathcal{R}/k = \mathcal{R}_t/k - \int_0^\infty F_t(r)(H-E)F_t(r)dr + \int_0^\infty \delta F(H-E)\delta F dr\,, \qquad \text{(V.3)}$$

where $H \equiv -d^2/dr^2 - V(r)$. Kato's important contribution was his ability to calculate upper and lower bounds for the error term. He begins by noting the following information about the error function δF;

$$\begin{aligned} (H-E)\delta F(r) &= (H-E)F_t(r) \\ \delta F(0) &= 0 \\ \delta F(r) &\sim \text{const} \times \cos kr \end{aligned} \qquad \text{(V.4)}$$

and examines the properties of the eigenfunctions and eigenvalues of the following eigenvalue problem,

$$[-H + E + \mu_n \rho(r)]u_n(r) = 0\,, \qquad \text{(V.5)}$$

where $u_n(r)$ satisfies the same boundary conditions as δF and where $\rho(r)$ is some suitably chosen weight function. The eigenvalue spectrum is discrete and denumerably infinite. If α and β are the smallest, in magnitude, positive and negative eigenvalues, respectively, then

$$-1/\beta \leqslant 1/\mu_n \leqslant 1/\alpha, \text{ for all } n\,. \qquad \text{(V.6)}$$

This equation is basic to determining upper and lower bounds on the error term.

Using the inequality (V.6), and substituting the functions δF and $1/\rho(-H+E)\delta F$ into the Parseval identities, which hold for any pair of functions, leads in a straightforward manner to

$$\frac{1}{\beta}\int[(-H+E)F_t]^2\frac{dr}{\rho} \geqslant \int \delta F(-H+E)\delta F dr \geqslant -\frac{1}{\alpha}\int[(-H+E)F_t]^2 dr/\rho\,. \qquad \text{(V.7)}$$

The inequality (V.7) gives a prescription for computing upper and lower bounds on the error term.

---

[86] L. Rosenberg and L. Spruch, Phys. Rev. **120**, 474 (1960).

In another interesting paper, Kato[87] has shown that the various variational principles of Hulthen, Kohn, and others, are essentially related to one another through the choice of the asymptotic normalization of the functions.

It should be remarked that the Kato method can only be applied to scattering problems in which the various angular momenta are uncoupled and if the scattering for a particular angular momentum can be completely characterized by one *real* phase shift. This essential requirement of the method remains in later applications.[80–84]

In their first paper, Spruch and Rosenberg[80] consider Eq. (V.3) in the limit as $k \to 0$. Then, $\lim k \to 0$ $\mathcal{R}/k \to -A$, the scattering length, and Eq. (V.3) reduces to

$$A = A_t + \int_0^\infty F_t(H)F_t dr - \int_0^\infty \delta F(H)\delta F dr\,, \tag{V.8}$$

while the asymptotic form, Eq. (III.23), for the $l = 0$ partial wave reduces to (with $C = 1$)

$$F(r) \backsim r + \mathcal{R}/k = r - A\,. \tag{V.9}$$

In this problem, Spruch and Rosenberg do not use the associated eigenvalue technique of Kato in order to obtain a bound on the error term. They note that since H is a positive definite operator on the space of square-integrable functions ($L > 0$), or for functions that approach some finite, possibly nonvanishing, constant at infinity ($L = 0$), then we have the important result

$$-\int \delta F(H)\delta F dr \leqslant 0 \tag{V.10}$$

and therefore

$$A - A_t - \int F_t H F_t dr \leqslant 0\,,$$

or

$$A \leqslant A_t + \int F_t H F_t dr\,. \tag{V.11}$$

Therefore, we obtain the result that any choice of the parameters in the trial function will yield an *upper* bound on A. The Kohn and Hulthen variational principles are two prescriptions for optimizing the choice of these parameters.

Spruch and Rosenberg[81] generalized Kato's[77] associated eigenvalue technique to apply to the scattering of a particle by a compound system. In this paper they treated low-energy positron scattering from atomic hydrogen. In Hylleraas[79] coordinates the Hamiltonian is $H = T + V$, where for zero total orbital angular momentum,

$$\begin{aligned} -2T &= \frac{1}{r_1^2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} \\ &\quad + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{\partial}{\partial p}(1 - p^2)\frac{\partial}{\partial p} \\ &= \frac{1}{r_1^2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} \\ &\quad + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}}\frac{\partial}{\partial r_1}\frac{\partial}{\partial r_{12}} \\ &\quad + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}}\frac{\partial}{\partial r_2}\frac{\partial}{\partial r_{12}} \end{aligned} \tag{V.12}$$

and

$$V/2 = \frac{1}{r_1} \pm \left(\frac{1}{r_2} - \frac{1}{r_{12}}\right),$$

where the upper plus sign is for electrons, and the asymptotic form of the wave function is given in Eqs. (III.20) and (III.23). The identity (III.38) for the first variation in I still applies with the volume integral

$$dv = dr_1\, r_2^2\, dr_2\, dp = r_1\, dr_1\, r_2\, dr_2\, r_{12}\, dr_{12}$$

The bound on the scattering length so obtained is justified only if (i) the eigenfunctions of the associated problem form a complete set; (ii) Levinson's theorem[88] is valid for scattering by a compound system; and (iii) no three-body bound state exists for the $e + \mathrm{H}$ system.[89] In another paper,[82] they were able to extend the method they had developed in the one-dimensional problem[80] to scattering by a compound target, to show that $\int \delta\Psi(H)\delta\Psi dv \leqslant 0$. Thus, the scattering length is given by the three-dimensional analog to (V.11). Spruch and Rosenberg[81] assumed two types of trial functions. The first class of trial functions is of the separable form, $g(r_2) \times f(r_1)$, which leads to the static approximation. They showed that the scattering length for the static problem A_s, say, provides an *upper bound* on the scattering length for the true problem. However, since this number turned out to be positive, it does not provide either an upper or lower bound on the cross section, see Eq. (III.57). In the second class of trial functions, they chose functions that depended on r_{12}, as well as r_1 and r_2. Since the scattering length satisfies a *minimum* principle, they simply varied their variational parameters and kept those parameters which gave

---

[87] T. Kato, Phys. Rev. **80**, 475 (1950).

[88] N. Levinson, Kgl. Danske Videnskab. Selskab, Mat.-fys, Medd. **25**, No. 9 (1949).

[89] C. Fronsdal and A. Ore, Physica **19**, 605 (1953).

TABLE X. Positron-hydrogen atom scattering lengths (units of a_0) as computed in several approximations.

A	Bound	Approximation	Reference	Information on σ
+0.5823	upper	static	81	
+0.582	upper	static	54	
+0.564	upper	strong coupling	54	
0.1704	upper	1*s*(H)-1*s*(positronium)	59	
—0.78	upper	variational	97	lower
—0.92	upper	*p*-wave distortion	110	lower
—1.397	upper	distortion included	81	lower
—2.10	upper	variational	93	lower
—3.06		1*s*(H)-1*s*(*p*), including dipole polarization	59	

the *least* value. They obtained a *negative* scattering length. Since it is an upper bound, this immediately yields a *lower* bound on the cross section. Furthermore, $A < 0$ implies that the positron is on the whole *attracted* to the hydrogen atom in contrast to all previous calculations, which had predicted an overall *repulsion*. Their results are given in Table X.

The extension of the above results, on deriving upper bounds on the scattering length, to the case where one or more composite bound states may exist, has been given by Rosenberg *et al.*[83] The essential problem is to estimate the error term, hopefully something as simple as the inequality (V.10). If such bound states exist, then the error function, $\delta\Psi(\mathbf{r}_1,\mathbf{r}_2)$, might contain components of the bound state wave functions, $u_\epsilon(\mathbf{r}_1,\mathbf{r}_2)$. This implies that $Hu_\epsilon = -\epsilon\, u_\epsilon$, where $\epsilon > 0$, which would give a *positive* contribution to the l.h.s. of (V.10) and possibly make the whole error term positive! However, if the error function is orthogonal to u_ϵ, i.e., $\int \delta\Psi u_\epsilon dv = 0$, then this positive contribution does not occur. Since $\delta\Psi \equiv \Psi_t - \Psi$, and the scattering states Ψ will be already orthogonal to u_ϵ, then to effect $(\delta\Psi,u_\epsilon) = 0$, we must construct trial functions which are orthogonal to u_ϵ.

The orthogonalization process can be carried out formally on $\delta\Psi$ and leads to (V.10) being replaced by

$$-\int \delta\Psi(H)\delta\Psi dv \leqslant \varepsilon\left[\int \Psi_t u_\epsilon dv\right]^2, \qquad (V.13)$$

where ε is the bound state energy, i.e., < 0. This inequality allows us to calculate rigorous upper bounds on A. The difficulty with this inequality is that u_ϵ is not known in general. This can be circumvented by using the Schwartz inequality, which unfortunately often leads to a considerable overestimate of the error term.

Using two theorems due to Hylleraas and Undheim,[90] Rosenberg *et al.*[83] were able to give an alternative method for calculating rigorous upper bounds on A. This method does not require either knowledge of the exact composite bound state function or use of the often crude Schwartz inequality.

In the problems of interest here, the only known composite bound state is that of the singlet state electron-hydrogen system,[91] i.e., the negative hydrogen ion H^-. Therefore, we shall be interested in the existence of a single composite bound state.

Let u_{ϵ_t} be a ground state trial function sufficiently accurate that its eigenvalue $\varepsilon_t < 0$ and (formally) orthonormal to $\delta\Psi$. Furthermore, let H_{ij} be a 2×2 matrix whose elements are defined by $\int u_{\epsilon_t}Hu_{\epsilon_t}dv$, $\int u_{\epsilon_t}H\delta\Psi dv$, etc. It then follows, from the Hylleraas-Undheim[90] theorems, that the eigenvalues of the matrix H_{ij} satisfy the relation

$$\varepsilon_1\varepsilon_2 \leqslant 0,$$

or

$$\int u_{\epsilon_t}Hu_{\epsilon_t}dv \int \delta\Psi H\delta\Psi dv - \left[\int u_{\epsilon_t}H\delta\Psi dv\right]^2 \leqslant 0, \qquad (V.14)$$

since the product of the eigenvalues of a matrix is equal to the determinant of the matrix. This inequality is valid even if $\delta\Psi$ is not orthogonal to u_{ϵ_t} which leads to the inequality

$$-\int \delta\Psi H\delta\Psi dv \leqslant \left[\int u_{\epsilon_t}H\Psi_t dv\right]^2 \Big/ \varepsilon_t, \qquad (V.15)$$

which in turn replaces (V.13) and so provides an upper bound on the scattering length,

$$A - A_t - 2\int \Psi_t H\Psi_t dv \leqslant \left[\int u_{\epsilon_t}H\Psi_t dv\right]^2 \Big/ \varepsilon_t,$$

or

$$A \leqslant A_t + 2\int \Psi_t H\Psi_t dv + \left[\int u_{\epsilon_t}H\Psi_t dv\right]^2 \Big/ \varepsilon_t. \qquad (V.16)$$

For a given form of the trial functions, Ψ_t and u_{ϵ_t}, the best choice of the variational parameters is such as to minimize the r.h.s. of (V.16) subject to $\varepsilon_t < 0$.

Rosenberg *et al.*[83] carried out an analysis of an earlier calculation by Borowitz and Greenberg[40] and obtained the first rigorous upper bound on the scattering length in the singlet state, see Table XI(a).

Assuming no composite bound state in the triplet state, the bound on the error term is given by the three-dimensional analog to (V.10). Hence, the *upper* bound on the triplet scattering length is given by the analog to (V.11), that is

$$^3A \leqslant {}^3A_t + 2\int {}^3\Psi_t(T + V - \varepsilon_H)\,{}^3\Psi_t dv. \qquad (V.17)$$

---

[90] E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930); and J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933).

[91] H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin), 240 (1957), Vol. 35.

TABLE XI. Summary of electron-hydrogen atom scattering lengths. The bounds quoted in these tables depend on the assumption that there is only one bound singlet state and no bound triplet state. Since these values are positive upper bounds, then no bound on the cross section can be given. Those results marked with an asterisk are not strict upper bounds since the contribution from H^- was neglected.

	A	Bound	Approximation	Reference
(a) Singlet	8.14	upper	variational, no distortion	83 (using 40)
	7.63	upper	variational, distortion included	83 (using 40)
	7.8	*	spherical symmetric part of S-wave equation	106
	8.095	*	$1s$, exchange	46
	8.05	*	$1s$-$2s$ exchange	54
	6.742	*	$1s$-$2s$-$2p$ exchange	64
	6.372	*	$1s$, exchange adiabatic	101
	6.23	upper	variational, distortion included	84
	6.17		effective range expansion about H^- in bound state	129
	5.965 ± .003	upper	variational, distortion included	93
	5.7	*	polarized orbital	103 (and 106)
	5.6	*	S-wave equation	106
(b) Triplet	2.35	upper	$1s$ exchange	46
	2.33	upper	$1s$-$2s$, exchange	54
	1.993	upper	$1s$, exchange adiabatic	101
	2.338		spherical symmetric part of S-wave equation	106
	1.91	upper	variational distortion included	84
	1.893	upper	$1s$-$2s$-$2p$, exchange	64
	1.7		polarized orbital	103 (and 106)
	1.768 ± .0002	upper	variational, distortion included	93
	1.76		S-wave equation	106

The right-hand side of this inequality is the Kohn-Hulthen variational estimate of ${}^3A$. Thus, the Kohn-Hulthen calculations[46,54,64] that have been performed, represent rigorous upper bounds on ${}^3A$ as well as variational estimates. This important fact, that (V.17) represents a bound on ${}^3A$, gives much more meaning to any calculated estimate. Its practical significance for variational calculations is immediately apparent since that set of parameters which gives a lower value to ${}^3A$ than other sets is the *best* set. Rosenberg *et al.*[84] have used these methods to obtain significantly smaller positive upper bounds than those estimated previously, see Table XI(b).

Until now, the discussion in this subsection has been concerned with zero-energy scattering (with the exception of the brief description of Kato's method). Several very important results on rigorous upper bounds on the scattering lengths for e^-H and e^+H systems have been quoted. In the remainder of the subsection we shall turn our attention to positive-energy scattering,[77,75,86] That is, we attempt to obtain bounds on the error terms of Eq. (V.3) and hence a bound on $\mathcal{R}/k = \tan \eta/k$. Since the initial kinetic energy $k^2 > 0$, then there will be a continuum of solutions of the Hamiltonian with energies below k^2, in addition to the composite bound states of the system. Therefore, if we follow the methods developed for $k^2 = 0$, a bound on $(1/k \cot \eta)^{-1}$ may be obtained by performing an infinite number of subtractions!

At the moment, no rigorous method has been given for calculating bounds for finite energies. Spruch and Rosenberg[75,86] seek to make the number of subtractions finite by considering a *fictitious* scattering problem with cutoff potentials. For small k^2, one would obtain few "positive-energy bound" states in the associated bound state problem. However, one would expect that the cutoff would have to be made at large distances in order not to neglect too much of the tail of the polarization potential. As the incident energy increases and the importance of the polarization potential decreases, one might expect to *decrease* the cutoff radius, but this gain would be "compensated" by having to subtract out more "positive-bound states." In any case, the bounds so obtained are not for the true problem.

(c) Applications

The important fact to emerge from the previous sub-section is that Kohn-Hulthen variational calculations provide rigorous upper bounds on the scattering lengths. As stressed earlier, this valuable piece of information means that the *best* trial function is the one which predicts the least upper bound. Spruch and his collaborators[81,83,84] have used this criterion and their results are given in Tables X and XI.

Schwartz[92] has carried out calculations of the elastic scattering of electrons from hydrogen atoms for $L = 0$. Schwartz bases his calculation on Eq. (III.40), writing $\mathcal{R} = \tan \delta$, which yields an upper bound on $\mathcal{R}/k$ in the limit as $k \rightarrow 0$, and a trial function

$$\Psi_t = \psi + \sum_i c_i X_i \, , \tag{V.18}$$

where ψ has the desired asymptotic form and where the localized trial function has the form

$$X_{mnp} = e^{-[\kappa(r_1+r_2)/2]} r_{12}^{m} (r_1^{n} r_2^{p} \pm r_1^{p} r_2^{n})/4\pi\sqrt{2} \, , \tag{V.19}$$

with $m + n + p \leqslant N$. Compared with Burke and Schey,[64] his triplet phase shifts differ by less than one percent, whereas the singlet phase shifts differ from three to ten percent for $k^2 < 0.25$. The scattering lengths[93] are quoted in Table XI and his phase shifts in Table XII.

TABLE XII. Electron-hydrogen atom partial-wave phase shifts calculated by a variational method,[93] row b and by Temkin's method,[106] row a.

k^2		Singlet	Triplet
0.0	a	5.6	1.76
	b	5.965	1.7686
0.0001	a	3.086	3.1237
0.0025	a	2.86	3.046
0.01	a	2.59	2.942
	b	2.553	2.9388
0.04	a	2.11	2.723
	b	2.0673	2.7171
0.09	a	1.74	2.516
	b	1.6924	2.4996
0.16	a	1.45	2.301
	b	1.4146	2.2938
0.25	a	1.23	2.112
	b	1.202	2.1046
0.36	b	1.041	1.9329
0.64	a	0.85	1.647
	b	0.886	1.643

Hara *et al.*[94] have also carried out a Hulthén variational calculation, in the limit of zero energy, for eight- and five-parameter trial functions. Their upper bounds are above those quoted by Schwartz. Saraph[95] has applied the Schwinger variational principle to the static exchange approximation[46] in order to compute estimates of the scattering lengths. For three-term polynomials, A_S coincided with John's result,[46] whereas A_t was above the upper bounds quoted in Table XI (b). Geltman[96] has also used the Hulthén-Kohn variational method in e^-H atom collisions allowing for virtual S-state excitation. His triplet phase shifts are very close to those of John,[46] while the singlet results differ slightly to give $A_S = 8.220$ compared with 8.095 from the static exchange approximation.

Allison *et al.*[97] have applied the Kohn and Hulthén variational methods to calculate the e^+H scattering length. They allowed for the dipole polarizability of the target atom by using a trial function which includes a term corresponding to the first-order perturbation of the atom due to the electric field of the positron. Their best result is quoted in Table IX and indicates over-all attraction between the positron and the atom at zero energy.

Moiseiwitsch[98] has generalized Hulthén's variational method to apply to the inelastic scattering of electrons by atoms. Since the variational calculations performed to date for inelastic processes have been exploratory and are approximations to the 1s-2s coupling method of Sec. IV (b) we shall not comment on the results.

We conclude this section by remarking that Rosenberg and Spruch[99] have generalized their techniques for estimating upper bounds on the elements of the $\mathcal{R}$ matrix for a fictitious problem with cut-off potentials.

VI. OTHER METHODS

(a) Adiabatic Theory

In the introduction, we remarked that the crucial theoretical problem is to make proper allowance for the distortion of the charge distribution of the atomic

---

[92] C. Schwartz, Ann. Phys. **16**, 36 (1961).

[93] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[94] Y. Hara, T. Ohmura and T. Yamanouchi, Prog. Theoret. Phys. (Kyoto) **25**, 467 (1961).

[95] H. E. Saraph, Proc. Phys. Soc. (London) **77**, 827 (1961).

[96] S. Geltman, Phys. Rev. **119**, 1283 (1960).

[97] D. C. S. Allison, H. A. J. McIntyre, and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **78**, 1169 (1961); B. H. Bransden, *ibid.* **79**, 190 (1962) using a perturbation method also computed a negative scattering length.

[98] B. L. Moiseiwitsch, Phys. Rev. **82** 753 (1951), see also H. S. W. Massey, and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A66**, 406 (1953); R. J. Huck, *ibid.* **A70**, 369 (1957); and N. Lynn, *ibid.* **73**, p. 515 (1959).

[99] L. Rosenberg and L. Spruch, *2nd International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 134; Phys. Rev. **125**, 1407 (1962).

electron produced by the projectile. In Sec. IV, spherical distortions and nonspherical distortions were introduced in a systematic way by including S states and P states, respectively, in the eigenfunction expansion of the total wave function. The question of convergence of the eigenfunction approach is deferred to Sec. VII. In the adiabatic theory, the attempt is made to allow for distortion using a simple physical picture.

This picture consists of two parts. In the first part we compute the quantum state of the atomic electron when under the influence of the external charge of the colliding particle. The fundamental assumption of the adiabatic theory is invoked at this stage of the method. It is assumed that the velocity of the impinging particle is so small that the distortion of the charge distribution of the atomic electron may be calculated by treating the projectile as a point charge at rest.[100] If the unperturbed atomic electron is in the ground stage $\psi(\mathbf{r}_1)$, say, then, using first-order perturbation theory, the atomic wave function will be

$$\psi_{\mathbf{r}_2}(\mathbf{r}_1) = \psi(\mathbf{r}_1) - \sum_{n,l}{}' \frac{V_{nl0,100}(\mathbf{r}_2)}{\epsilon_n - \epsilon_1} \psi_{nl0}(\mathbf{r}_1) \, . \tag{VI.1}$$

That is, the atomic wave function depends, parametrically, on the position $\mathbf{r}_2$ of the incident particle. The prime denotes $n \neq 1$.

In the second part, the problem is to calculate the function which describes the motion of the projectile (the asymptotic form of this function yields the elements of the $\mathcal{R}$ matrix and hence the cross section) scattered by the target in the *perturbed* quantum state. This can be done, for example, by modifying the trial function in the exchange approximation, see Sec. IV (a), by replacing $\psi(\mathbf{r}_1)$ by Eq. (VI.1) and deriving Euler-Langrange equations which would replace Eq. (IV.1). The principal feature of this approximation is that when the target and projectile are far apart, a *dipole* moment is *induced* in the atom. Thus, the colliding particle moves in an induced dipole potential $V_p \sim \alpha/r^4$, where α is the atomic polarizability, $\alpha_H = 4.5$. As outlined earlier [Sec. III(a)], Castillejo *et al.*[27] have shown that this theory can be applied for incident energies which are too small for inelastic collisions to occur and for large separations.

Martin, Seaton, and Wallace[101] have used the adiabatic theory in electron-hydrogen atom collisions. They observe that since W^{ls} and V^l in Eq. (IV.1) go to zero exponentially for large r, the function F^{ls}, in the exchange approximation, does *not* satisfy the polarizability equation (III.10) at large r. In the first part of their paper, they introduce V_p *ad hoc* into Eq. (IV.1). The resulting differential equations *cannot* be derived from a variational principle. Therefore, the values of the scattering length computed in this so-called "exchange-adiabatic approximation" do not provide a bound on the true scattering length.

Martin *et al.* have also followed the second part of the procedure outlined above and substituted Eq. (VI.1) into the variational principle (III.39). However, they did *not* solve the resulting Euler-Lagrange equation. Instead they derived an expression for the scattering length which they evaluated using the functions from the exchange approximation. Their upper bounds are quoted in Table XI. It must be pointed out that these values are upper bounds to the true e^-H problem only if the adiabatic assumption is valid.

Dalgarno and Lewis[102] have shown that in the limit as $r_1 \rightarrow \infty$ and $r_1 > r_2$, the second term in Eq. (VI.1) is given by

$$\sum_{l=1}^{\infty} \frac{2}{r_2^{l+1}} e^{-r_1} \left[\frac{r_1^{l+1}}{l+1} + \frac{r_1^{l}}{l} \right] \frac{P_l(\cos\theta)}{(4\pi)^{\frac{1}{2}}} \, , \tag{VI.2}$$

where $\cos\theta = \hat{r}_1 \cdot \hat{r}_2$. The associated Euler-Lagrange equation (neglecting those terms which are quadratic in the perturbation) has been derived and solved by Temkin and Lamkin[103] retaining the $l = 1$ terms in Eq. (VI.2). They solved the resulting second-order ordinary integro-differential equation using the noniterative technique of Omidvar[50] and Percival (see Marriott[55]). Their scattering lengths are given in Table XI.

The induced dipole potential strength α is shown by Temkin and Lamkin to have the form

$$\begin{aligned} \alpha = 4.5 - \exp(-2r)[2r^5/3 + 3r^4 + 3r^3/2 \\ + 9r^2/4 + 9r/4 + 9/8] \, , \end{aligned} \tag{VI.3}$$

that is, it is a function of r.

The connection between the method of perturbed stationary states[1] and polarized orbitals[28] is now clear. The former is characterized by the formal expression, Eq. (VI.1), and the calculation of Martin *et al.* is an application of that method, retaining only the first term of the infinite sum. The latter is charac-

---

[100] N. F. Mott and I. N. Sneddon, *Wave Mechanics and its Applications* (Oxford University Press, New York, 1948).

[101] V. M. Martin, M. J. Seaton, and J. B. G. Wallace, Proc. Phys. Soc. (London) **72**, 701 (1958); see also B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, *ibid.* **71**, 877 (1958).

[102] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A**233**, 70 (1955).

[103] A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

terized by taking the first term of Eq. (VI.2), which can be regarded as an infinite sub-sum of (VI.1).

Massey *et al.*[59] have carried out calculations on the e^+H problem in the spirit of the adiabatic approximation. They have introduced, *ad hoc*, the induced dipole polarization potential α/r^4 [where α is given by Eq. (VI.3)] into both Eq. (IV.2) and (IV.8). The phase shifts of these calculations are given in Table III and the scattering lengths are quoted in Table X.

(b) The *S*-Wave Equation

It has been observed in Eq. (V.12), that the Hamiltonian for $L = 0$ total orbital angular momentum has a particularly simple form. That is, the *S*-wave Schrödinger equation reduces to a *single* three-dimensional second-order partial differential equation. This fact has been exploited by Spruch and his collaborators in deriving rigorous upper bounds on the scattering length. Temkin[104–106] has also studied this equation for the e^-H problem for $k^2 < 0.75$. His method is an extension of that due to Luke *et al.*[107]

Temkin[104] expands the total wave function for the e^-H system, $\Psi(r_1,r_2,p)$, where $p \equiv \hat{r}_1 \cdot \hat{r}_2$ in terms of Legendre polynomials with argument p. In this way, he replaces Eq. (III.5) with a different infinite set of coupled equations.[104] For $k^2 < 0.75$, the scattering can be characterized by a single real parameter, the phase shift δ, which enters the problem via the asymptotic boundary condition as $r_2 \to \infty$. The requirement that the total wave function must be either symmetric or antisymmetric under the exchange of the two electrons imposes the same requirement on $\Phi_l(r_1,r_2)$, which implies that the problem need only be solved in the region $r_2 \geqslant r_1$. The different symmetries of the singlet and triplet states is manifest in different boundary conditions along $r_1 = r_2$. Finally, the condition that $\Phi_l(0,r_2) = 0$ concludes the specification of the problem, which is to be solved in some approximate way.

Temkin[104,106] defines a zero-order approximation by considering the equation for $l = 0$ only and neglecting the coupling terms. The solution to this truncated equation he labels $\Phi_0^0(r_1,r_2)$, with a phase shift δ_0, which is related to the true phase shift δ by

$$\sin(\delta - \delta_0) = -\frac{1}{k}\sum_{l=1}^{\infty}\frac{2}{(2l+1)^{\frac{1}{2}}}\int_0^{\infty} dr_2 \int_0^{r_2} dr_1 \times \Phi_0^0 \frac{r_1^{\,l}}{r_2^{\,l+1}}\, \Phi_l(r_1,r_2)\,. \tag{VI.4}$$

Starting from this result, Temkin[105] has derived an expansion for $k \cot \delta$ which has precisely the linear term in k given by O'Malley *et al.*[41] for the idealized problem of a particle scattered by a $-\alpha/r^4$ potential, see Eq. (III.56). Furthermore, the quantitative effect of the long range tail on the scattering length is given by

$$A = A(R) - \alpha(1/R - A/R^2) + 0(1/R^3)\,, \tag{VI.5}$$

where $A(R)$ is an approximation to A.

The connection of Temkin's approach to the $L = 0$ problem, with the eigenfunction expansion approach developed in Secs. III and IV can be demonstrated by restricting the sum over L in Eq. (III.20) to the $L = 0$ term and noting that

$$\mathcal{Y}^0_{0 l_1 l_2}(\hat{r}_1,\hat{r}_2) = (-1)^l (2l_1 + 1)^{1/2} P_{l_1}(\hat{r}_1 \cdot \hat{r}_2)/4\pi\,. \tag{VI.6}$$

Hence the expansion (III.20) becomes

$$\Psi^{\Gamma'}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{r_1 r_2}\sum_{l_1} P_{l_1}(\hat{r}_1\cdot\hat{r}_2)\sum_n R_{nl_1}(r_1)F^{\Gamma'}_{nl_1}(r_2)\,, \tag{VI.7}$$

which is identically the form used by Temkin if we expand his Φ_n in terms of the radial hydrogen eigenfunctions. Thus, it is immediately clear that those calculations discussed in Sec. IV (a) and IV(b) which only include *S* states ($l_1 = 0$), are *approximations* to Temkin's δ_0.

It has been stressed repeatedly in this review that *S* states do not contribute to the long range interaction between atom and projectile. Hence, δ_0, considered as a function of r_2, will quickly assume its asymptotic form in contrast to δ, which will have contributions from the $l_1 > 0$ terms. We refer the reader to Temkin's original paper[106] for his technique for solving the zero-order problem and evaluation of the multipole corrections $l > 0$, as well as the connection with the corresponding terms in the adiabatic approximation. Temkin's scattering lengths and phase shifts are given in Tables XI and XII, respectively.

It is worth noting that the expansion of Φ_{l_1} in terms of the hydrogenic wave functions in Eq. (VI.7) is only one of many possible expansions. Any convenient complete set of functions could be used. In the next subsection we consider such an alternative—Sturmian functions.

(c) Sturmian Functions

We should like to emphasize that the principal advantages of the system of integro-differential

---

[104] A. Temkin, Phys. Rev. Letters **4**, 566 (1960).
[105] A. Temkin, Phys. Rev. Letters **6**, 354 (1961).
[106] A. Temkin, Phys. Rev. **126**, 130 (1962).
[107] P. J. Luke, R. E. Meyerott and W. W. Clendenin, Phys. Rev. **85**, 401 (1952); see also G. Breit, *ibid.* **36**, 383 (1930).

equations, (III.43) and (III.44), obtained by expanding the total wave function in terms of the eigenfunctions of the atomic systems, is in the physical interpretation of the solutions to these equations, see Sec. III (b). However, we could perform a separation of variables, such as (III.2) or (VI.7), by using *any* complete set of functions. In general, therefore, the expansion coefficients would not be related in a simple manner to the cross sections for the various possible physical processes. Therefore, it would be necessary to re-expand in terms of the eigenfunctions of the atomic systems. For such an expansion to be useful, we would have to know that its convergence was faster than the corresponding eigenfunction expansion.

Rotenberg[108] has looked into the possibility of using Sturmian functions[109] as an expansion basis; he obtained a negative scattering length in the e^+H problem. Rotenberg proposes to replace Eq. (III.20), for a given LM_L, by

$$\Psi^{LM_L} \equiv \sum_{nl_1l_2} \mathcal{Y}^{M_L}_{Ll_1l_2}(\hat{r},\hat{r}_\alpha) S_{nl_1}(r) G_{nl_1l_2}(r_\alpha) \,, \tag{VI.8}$$

where the Sturmian functions S_{nl_1} satisfy an equation analogous to the radial equation of the hydrogen atom. The difference is that the binding energy (chosen to be that of the ground state of the target) is kept constant while the coupling strength is varied. Thus $S_{10}(r) \equiv R_{10}(r)$ of the hydrogen atom; no other S_{nl} corresponds to a physical wave function. Each S_{nl} is identified with a solution to the radial equation with $(n - 1)$ nodes, hence the set of functions is denumerably infinite.

Qualitatively, we can imagine that the continuum of the atomic expansion has been absorbed in the Sturmian functions for $n > 1$. From a practical point of view, due to the finite size of computing machines, it will be possible only to include a few terms even from the denumerably infinite set. Hence, so far as the atomic-scattering problems are concerned, we can again expect to allow only partially for the effect of the continuum. In order to make further allowance for the continuum, Rotenberg proposes to antisymmetrize the total wave function, which is equivalent to expanding the "remainder terms" as discussed in Sec. III (c).

Substituting (VI.8) into the Schrödinger equation (III.1) results in systems of second-order differential or integro-differential (if one antisymmetrizes or includes positronium formation) equations for the expansion functions $G_{nl_1l_2}$.

We shall conclude this subsection by describing yet another expansion for Ψ^{LM_L}, which has been proposed by Ruffine and Borowitz[110] for the e^+H problem. The principal aim of this method is to construct a total wave function which includes the multipole distortive effects discussed previously. These authors write either Eq. (III.42) or Eq. (VI.8) in the form

$$\Psi^{LM_L} = \mathcal{Y}^{M_L}_{L0L}\psi_{100}(r)F_{10L}(r_\alpha) + \sum_{nl_1l_2}{}' \mathcal{Y}^{M_L}_{Ll_1l_2} S_{nl_1} G_{nl_1l_2}$$

and approximate the radial part of the second term by a product of two unknown functions, say, $u(r_1)$ and $v(r_2)$. They use this approximate total wave function in the variational principle (III.39), and deduce Euler-Lagrange equations involving F, u, and v.

Numerical calculations have been carried out for $L = 0 = k^2$ and $l_1 = 1$ only, that is allowing for p-wave distortion. Ruffine and Borowitz obtain a negative scattering length indicating that there is an overall attraction between the incident positron and atom. Their result is given in Table X.

(d) **Optical Model**

The basic assertion of the optical model method is that there exists an equivalence between a many-body problem and a one-body problem.[111] This equivalence is represented by the optical potential which is inserted into a single-body equation to yield the phase shift and cross section in the usual manner. The major part of the work is thus concerned with the evaluation of the optical potential. In the region of large r the optical potential is given exactly by the adiabatic approximation. For small distances the potential becomes nonlocal and extremely difficult to evaluate. Usually, therefore, some physically reasonable cutoff of the potential, such as suggested by Buckingham,[112] is used. The resultant phase shift can then be improved by a variational technique. This method has been used by Lippmann and Schey[113] and also by Mittleman and Pu[114] to calculate elastic e^-H

---

[108] M. Rotenberg Ann. Phys. (N. Y.) (to be published).

[109] E. L. Ince, *Ordinary Differential Equations* (Dover Publications, Inc., New York 1956) Chap. X.

[110] R. Ruffine and S. Borowitz, *2nd International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 144.

[111] K. M. Watson, Phys. Rev. **105**, 1388 (1957); M. H. Mittleman and K. M. Watson, *ibid.* **113**, 198 (1959); B. A. Lippmann, M. H. Mittleman, and K. M. Watson, *ibid.* **116**, 920 (1959).

[112] R. A. Buckingham, Proc. Roy. Soc. (London) A**160**, 94 (1937).

[113] B. A. Lippmann and H. M. Schey, Phys. Rev. **121**, 1112 (1961).

[114] M. H. Mittleman, Ann. Phys. (N. Y.) **14**, 94 (1961); M. H. Mittleman and R. T. Pu (private communication).

scattering below about 12 eV. It is interesting to note that the calculations of Martin *et al.*[101] and Temkin[28] have also been carried out within the framework of an optical model. The optical potential becomes complex above the threshold for inelastic scattering. The imaginary part can be used to evaluate the excitation cross section.[114] However, a better method of treating the excitation cross sections is to use an optically modified close-coupling approximation. It can be shown[115] that the unmodified close-coupling approximation is the lowest order approximation to a suitable optical-potential set of equations.

By definition, the optical-model wave function is the projection of the total wave function Ψ in Eq. (III.2) onto the ground-stage hydrogen wave function

$$F_1(\mathbf{r}_2) \equiv [\psi_1(\mathbf{r}_1),\Psi(\mathbf{r}_1\mathbf{r}_2)] \qquad \text{(VI.9)}$$

and the optical model potential U is defined

$$U(\mathbf{r}_2)F_1(\mathbf{r}_2) \equiv (\psi_1(\mathbf{r}_1),V\Psi(\mathbf{r}_1\mathbf{r}_2)) . \qquad \text{(VI.10)}$$

If exchange is neglected we can write the optical potential (VI.10) in the form

$$U_{11}(\mathbf{r}_2) = V_{11}(\mathbf{r}_2) + \sum_{n\neq 1} V_{1n}\frac{1}{E - T_2 - E_n + i\eta} V_{n1} + \cdots, \qquad \text{(VI.11)}$$

where E is the total energy of the system, T_2 is the kinetic energy of the scattered electron, and E_n is the energy of the nth hydrogen level. V_{nm} is given by Eq. (III.6). The first term $V_{11}(\mathbf{r}_2)$ in (VI.11) is just the screened Coulomb interaction of Eq. (IV.2), while the second term gives asymptotically the long range dipole interaction α/r^4. The problem of estimating $U_{11}(r_2)$ for large r_2 has been discussed in Secs. IIIa and VIa in the adiabatic limit $E - T_2 \simeq E_1$.

The presence of exchange can be taken into account by replacing V in (VI.11) by $RV(1 \pm P_{12})R$. Here R is an ordering operator among the hydrogen states, and P_{12} is the space-exchange operator for electrons 1 and 2. The orthogonality of the triplet wave function to the hydrogen-atom ground state is automatically ensured by the $(1 - P_{12})$ operator. The details of the calculation of $U_{11}^{\pm}(r_2)$ in this case have been given by Mittleman.[114] His triplet phase shifts are in good agreement with those obtained by the close-coupling method. Lippmann and Schey,[113] in their work, did not introduce the $(1 \pm P_{12})$ operator. Instead they obtained the required orthogonality by the novel[76] technique of introducing an inhomogeneous term representing the exchange interaction, in the differential equation. The strength of this term was adjusted to give the orthogonality. Having calculated F_1, Lippmann and Schey used this function to construct a trial function which they put in the variational principle (III.39). Their result for the triplet scattering length is larger than those given in Table XI (b).

If N hydrogen states are closely coupled then, neglecting exchange, we obtain a set of equations corresponding to (III.4). It can be shown[115] that if the potential U in this equation is defined analogously to (VI.11), i.e.,

$$U_{nm}(\mathbf{r}_2) = V_{nm}(\mathbf{r}_2) + \sum_{j>N} V_{nj}\frac{1}{E - T_2 - E_j + i\eta} \times V_{jm} + \cdots \quad n,m \leqslant N , \qquad \text{(VI.12)}$$

then the resultant set of equations is exact. V_{nm} is the usual close-coupling potential while higher order terms in (VI.12) allow for transitions to states not included in the closely coupled set. No results for this method have been reported yet.

(e) Impulse Approximation

Akerib and Borowitz[116] have applied the impulse approximation to the e^{-}H problem at the low energies of interest here, although on general arguments one would not expect it to be accurate for incident electrons under 150 eV. The central idea is to derive approximate expressions for the full scattering amplitudes.

We begin by converting Eq. (III.4), together with the asymptotic boundary condition (III.8), into an integral equation and considering the scattered part of the wave function only,

$$F_m(\mathbf{r}_\alpha) \backsim -\frac{\exp(ik_m r_\alpha)}{4\pi r_\alpha}\int dr'_\alpha \exp(-i\mathbf{k}_m\cdot\mathbf{r}'_\alpha) \times \int d\mathbf{r}\psi_m^*(\mathbf{r})U\Psi(\mathbf{r},\mathbf{r}'_\alpha) . \qquad \text{(VI.13)}$$

For the e^{-}H problem, if electron 2 is incident, then the *direct* scattering amplitude f_m is obtained by assigning $\mathbf{r}_1$ to $\mathbf{r}$ and $\mathbf{r}_2$ to $\mathbf{r}_\alpha$, while the *exchange* scattering amplitude g_m is obtained by assigning $\mathbf{r}_1$ to $\mathbf{r}_\alpha$ and $\mathbf{r}_2$ to $\mathbf{r}$.

The basic assumption of the impulse approximation is that the interaction between the bound particles can be "turned off" during the collision. This assumption can be incorporated into Eq. (VI.13) by assuming that $\Psi(\mathbf{r},\mathbf{r}_\alpha)$ represents the interaction of the incident particle with a *free* electron, whose momentum distribution is given by the Fourier trans-

---

[115] M. H. Mittleman and R. T. Pu, Phys. Rev. 126, 370 (1962).

[116] See reference 24a.

form of the ground-state wave function of hydrogen,

$$\Psi(\mathbf{r},\mathbf{r}_\alpha) \approx \frac{1}{(2\pi)^{\frac{3}{2}}}\int d\mathbf{k}_1 g_0(\mathbf{k}_1) \exp\{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}\} \times \psi_{\frac{1}{2}(\mathbf{k}_1-\mathbf{k}_2)\rho}\,, \qquad \text{(VI.14)}$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\rho \equiv \mathbf{r}_1 - \mathbf{r}_2$. Substituting (VI.14) into (VI.13) gives explicit expressions for the amplitudes f_m and g_m from which it is possible to calculate the cross section for elastic scattering[117] ($m = 1$) as well as excitation to the state m from

$$\sigma_m = (k_m/k_1)[\tfrac{1}{4}|f_m + g_m|^2 + \tfrac{3}{4}|f_m - g_m|^2]\,. \qquad \text{(VI.15)}$$

We refer the reader to Akerib and Borowitz[116] for the technique of evaluating the integrals appearing in the scattering amplitudes. The results of calculations carried out in this approximation are discussed in Sec. VII.

The ionization cross section, see Eq. (VI.22), has been computed by these authors using the impulse approximation values for f and g. This calculation is of particular interest, since it is the only theoretical estimate of the total-ionization cross section, with the exception of Born approximation values.

(f) Dispersion Relations

Dispersion relations are expressions which relate the real and imaginary parts of a scattering amplitude.

It should be remarked at the outset that dispersion relations have *not* been used to date in the same role as the other theoretical methods described in this review. That is, they have not been used to compute a purely theoretical estimate of some quantity which can then be compared with experiment. Instead, they have been used to analyze the results of two conflicting experiments.[8,10]

Gerjuoy and Krall[118] have *conjectured* dispersion relations for the direct and exchange amplitudes, see Eq. (VI.13), in the e^-H problem. The assumptions, from which the dispersion relations are deduced, are consistent with what is known about the Green's function for the one-body problem.[119] It is *assumed*[118] that the Green's function of the complete Hamiltonian, $(H - k^2 + 1 - i\epsilon)^{-1}$ (see reference 120 for notation), (a) has one pole, at a negative real energy, corresponding to the known bound singlet state of the hydrogen ion; (b) has branch points at each energy k_i^2 corresponding to the threshold of a new reaction (for example, at $k^2 = 0$, the threshold for elastic scattering, $k^2 = 0.75$ the threshold for excitation of the $n = 2$ state, etc); (c) is single valued and analytic (except at the pole and branch cut along the positive real axis) over the complex k^2 plane.

These assumptions lead to dispersion relations for the *forward* ($\theta = 0$) scattering amplitudes, $f^i(0,k^2)$, where i distinguishes direct ($i = d$) and exchange ($i = e$) scattering. σ_t the total cross section is related to these amplitudes (using the optical theorem, see, for example, Schiff[121]) by

$$\operatorname{Im}[f^d(0,k^2) - f^e(0,k^2)/2] = k\sigma_t(k^2)/4\pi\,. \qquad \text{(VI.16)}$$

From the dispersion relations for f^i, we can construct the dispersion relation

$$\operatorname{Re}(f^d - f^e/2) = (f^d - f^e/2)_{\text{Born}} - R/2 + \frac{\mathcal{P}}{4\pi}\int_0^\infty dk'^2 \operatorname{Im}(f^d - f^e/2)/(k'^2 - k^2)\,, \qquad \text{(VI.17)}$$

where $\mathcal{P}$ denotes the principal value of the integral, and R is the residue at the pole.

The relation (VI.17), together with the assumption of positive scattering lengths in the e^-H problem has been used to deduce

$$(1/2\pi^2)\int_0^\infty \sigma_t(k)dk \leqslant 7.500\,, \qquad \text{(VI.18)}$$

where σ_t is the measured *total* cross section.

(g) Born Approximation

We conclude this brief survey of the various theoretical methods currently being used on the e^-H and e^+H problems with some remarks on the most famous of all collision-theory approximations. We shall not attempt to summarize the results of all the calculations, on the problems of interest here, which have been carried out in this approximation. In the following paragraphs we discuss, in a qualitative way, the region of validity of the approximation; the calculation of $Q(1S\text{-}2P)$ and a Coulomb modified Born approximation calculation of the ionization cross section.

The Born approximation[122] is an approximation which assumes weak coupling between pairs of states. That is, in calculating transition probabilities, the initial and final scattered wave functions can be ap-

---

[117] R. Akerib, *2nd International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 147.

[118] E. Gerjuoy and N. A. Krall, Phys. Rev. **119**, 705 (1960); N. A. Krall and E. Gerjuoy, *ibid.* **120**, 143 (1960).

[119] A. Klein and C. Zemach, Ann. Phys. (N. Y.) **7**, 440 (1959).

[120] B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950); see also M. Gell-Mann and M. L. Goldberger, *ibid.* **91**, 398 (1953).

[121] L. I. Schiff, Prog. Theoret. Phys. (Kyoto) **11**, 288 (1954).

[122] M. Born, Z. Physik **38**, 803 (1926).

proximated by plane waves. In general, this approximation is *not* valid at low energies, where the scattered particle spends an appreciable time near the atom. At low energies more sophisticated approximations, allowing for distortions both of the atom and of the scattered wave function, are required. However, in certain circumstances, the Born approximation may be used at these energies, with accuracy, and a considerable saving of machine time. For example, it can give accurate partial-wave cross sections for transitions involving high angular momentum states of the scattered particle that is far from the atom during the whole collision time and consequently both its potential and exchange interactions are small. This is just the criterion for the validity of the Born approximation.

Perhaps the most important application of this method is the calculation of high angular momenta partial wave cross sections in optically allowed transitions (e.g., 1*s*-2*p*). Here the long range of the interaction potential which is proportional to r^{-2}, see Eq. (VI.2), implies that many partial waves are of importance in the collision. Seaton and co-workers[123] used this method to calculate partial wave $\mathcal{R}$-matrix elements and cross sections involved in transitions between the 1*s*, 2*s*, and 2*p* states of atomic hydrogen induced by electron impact. These results, supplemented by more accurate estimates of the low partial waves, such as that given by the close-coupling approximations, are expected to provide accurate theoretical values for the cross sections.

The second Born approximation for the full scattering amplitude may be expected to give accurate cross sections in an intermediate energy region, where too many partial waves are involved to make feasible, numerically speaking, the usual close-coupling approximation and where the first Born approximation for the full amplitude is still inaccurate. For hydrogen, this energy range is approximately 50–200 eV. The method has been used, allowing for virtual transitions to the 1*s*, 2*s*, and 2*p* intermediate states, by Kingston *et al.*[124] to estimate the 1*s*-2*s* electron hydrogen transition cross section in the energy range 13.6–216 eV. Agreement was obtained with the close-coupling approximation for energies in excess of 100 eV.

The modification of the Born approximation to allow for electron exchange, suggested by Oppenheimer,[125] has not been of corresponding value. This is probably because for those energies and angular momenta where exchange becomes significant, the scattered electron must penetrate the atom enough to invalidate, as a rule, the main criterion of the Born approximation, that is, that the distortion both of the atom and of the scattered wave is negligible.

In deriving the Born approximation partial wave cross sections in electron hydrogen atom scattering, Seaton *et al.*[123] write for the Born $\mathcal{R}$-matrix elements

$$\mathcal{R}^{L}_{k_n n l_1 l_2, k_n' n' l_1' l_2'} = -2(k_n k_n')^{1/2}[\Psi^{LM}_{k_n n l_1 l_2}(\mathbf{r}_1\mathbf{r}_2),$$
$$\times\ (1/r_{12} - 1/r_2)\Psi^{LM}_{k_n' n' l_1' l_2'}(\mathbf{r}_1\mathbf{r}_2)]\,, \qquad \text{(VI.19)}$$

where $\Psi^{\mathrm{LM}}_{k_n n l_1 l_2 (\mathbf{r}_1, \mathbf{r}_2)}$ are the basis functions in the summation in Eq. (III.20), omitting the spin function and approximating the radial functions by

$$F^{\Gamma}(r) \approx (\pi r/2)^{1/2} \cdot J_{l_2+1/2}(k_\alpha r) \qquad \text{(VI.20)}$$

The corresponding cross section contribution is obtained by substituting the value obtained for $\mathcal{R}$ from Eq. (VI.19) into Eqs. (III.31) and (III.32) after using

$$T = 2i\mathcal{R}/(1 - i\mathcal{R})\,. \qquad \text{(VI.21)}$$

Seaton *et al.* define another approximation in which the T matrix is defined by $T = 2i\mathcal{R}$. This latter approximation corresponds to the usual Born approximation for the full amplitude and using it (III.32) can be summed to give the Born cross section formula (See reference 1, p. 119). However, the first method has the advantage that unitarity is satisfied. Furthermore, if all $\mathcal{R}$-matrix elements connecting a closely coupled set of levels (e.g., 1*s*, 2*s*, and 2*p*) are evaluated using Eq. (VI.19) and the T matrix is calculated using Eq. (VI.21) (assuming that all other $\mathcal{R}$-matrix elements are zero), then some allowance is automatically made for second- and higher-order transitions between the closely-coupled levels. In practice, it is found that the first method gives better results for lower angular momenta than the second, but both reduce to the same approximation for high angular momenta.

Massey and Mohr[126] have calculated the direct amplitude for ionization using the Born approximation. Geltman[127] has developed a modified form of the Born approximation to calculate both the direct f and exchange g amplitudes for ionization. He has calculated only the S-wave contribution to the cross section.

The differential cross section for an ionizing colli-

---

[123] M. J. Seaton, Proc. Phys. Soc. (London) **77**, 174 (1961); **77**, 184 (1961); J. Lawson, W. Lawson, and M. J. Seaton, *ibid.* **77**, 192 (1961); V. M. Burke and M. J. Seaton, *ibid.* **77**, 199 (1961).

[124] A. E. Kingston, B. L. Moiseiwitsch, and B. G. Skinner, Proc. Roy. Soc. (London) A**258**, 254 (1960).

[125] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[126] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A**140**, 613 (1933).

[127] S. Geltman, Phys. Rev. **102**, 171 (1956).

sion in which the ejected electron is moving with momentum in the range $\mathbf{k}$ to $\mathbf{k} + d\mathbf{k}$, while the scattered electron has momentum in the range $\mathbf{c}$ to $\mathbf{c} + d\mathbf{c}$, is[116]

$$I_{0k} d\mathbf{k}\, d\mathbf{c} = \frac{1}{q} \{\tfrac{1}{4}|f + g|^2 + \tfrac{3}{4}|f - g|^2\} d\mathbf{k}\, d\mathbf{c}\,, \tag{VI.22}$$

where $\mathbf{q}$ is the momentum of the incident electron. The transition cross section into a final state in which the energy of the electron, no matter whether scattered or ejected since they are indistinguishable, is within the interval $d\mathcal{E}$ is[128]

$$\sigma(\mathcal{E},E - \mathcal{E})d\mathcal{E} \equiv \iint I_{0k} d\mathbf{k}\, d\mathbf{c} \cdot d\mathcal{E}\,, \tag{VI.23}$$

where E is the total energy. Since the maximum energy an electron can take away is $E/2$, then the total ionization cross section

$$Q = \int_0^{E/2} \sigma(\mathcal{E},E - \mathcal{E})d\mathcal{E} = \tfrac{1}{2}\int_0^{E} \sigma(\mathcal{E},E - \mathcal{E})d\mathcal{E}\,, \tag{VI.24}$$

having used[128] $\sigma(\varepsilon,E - \varepsilon) = \sigma(E - \varepsilon,\varepsilon)$. Since Geltman[127] omitted the factor of 1/2 in Eq. (VI.24), then his results must be divided by two.

In Geltman's method, the scattering amplitudes involve radial integrals over functions A_{lm} defined by

$$\int \psi_\kappa^*(\mathbf{r})\, \frac{1}{|\mathbf{r} - \mathbf{r}'|}\, \Psi(\mathbf{r},\mathbf{r}')d\mathbf{r} \equiv \sum_{lm} A_{lm}(r')Y_{lm}(\hat{r}')\,, \tag{VI.25}$$

where ψ_κ are the continuum wave functions of the hydrogen atom. The Born approximation is introduced by approximating the over-all wave function Ψ by the initial state (product of ingoing plane wave and wave function for the hydrogen atom in a $1S$ state).

An improved approximation would be to substitute for Ψ $(\mathbf{r},\mathbf{r}')$ the values computed by the methods of Sec. IV. Such a calculation would provide further information on the convergence of the eigenfunction technique by examining the effect of including more and more excited states in Ψ.

VII. DISCUSSION OF RESULTS

(a) Scattering Lengths

The concept of scattering length is of considerable importance in the class of problems of interest in this review. The rigorous theorems on extrema principles for scattering lengths, discussed in Sec. V, allow us to state which is the better of two approximate calculations. It is stressed, that this definitive assessment of the relative merits of different theoretical results can be made without appeal to experiment.

These theorems have established the very important role of the long-range induced dipole polarization potential α/r^4 at very low energies. Furthermore, when this potential is taken into account, the scattering length can be defined only for the $l = 0$ partial wave; the scattering length for $l \geqslant 1$ does not exist! Under these conditions, we recall that the S-wave phase shift is given by Eq. (III.56) and is seen to contain terms in k and $k^2 \log k$.

However, if an approximate solution to the scattering problem is considered, which neglects the polarization potential [see Secs. IV (a) and IV (b)], then a scattering length can be defined for all partial waves [for $l = 0$, see Eq. (III.49)].

Positrons. The positron scattering lengths calculated by different methods are collected together in Table X. At the time of the Boulder Conference in June, 1961, there existed the basic question as to whether low energy positrons were attracted (negative scattering length) or repelled (positive scattering length) by the target hydrogen atom. Furthermore, if the interaction was attractive, what was the precise mechanism producing this effect? Calculations based on the eigenfunction expansion approach[45,54] supported the repulsive interaction, while the variational calculation of Spruch and Rosenberg[81] showed that the interaction must be attractive; "must," since the latter calculations gave a lower upper bound for the scattering length than the former. However, it was not clear which terms in the variational trial function were responsible for the attraction. Subsequent calculations by Massey *et al.*[59] showed that neither virtual positronium formation into the $1S$-state, nor virtual excitation of the $2P$ state of atomic hydrogen could produce a negative phase shift (attractive force) at low energies. However, all calculations, whether static, strong-coupling or virtual positronium, which included the dipole polarizability, yielded positive S-wave phase shifts. That is, there exists an over-all attraction between positrons and hydrogen atoms at energies below a few volts.

The results of Table X are strong evidence in favor of including dipole polarization in very low energy atomic collision problems. These results also indicate that a straightforward application of the eigenfunction expansion method may yield results which are even qualitatively incorrect.

Electrons. The singlet and triplet scattering lengths,

---

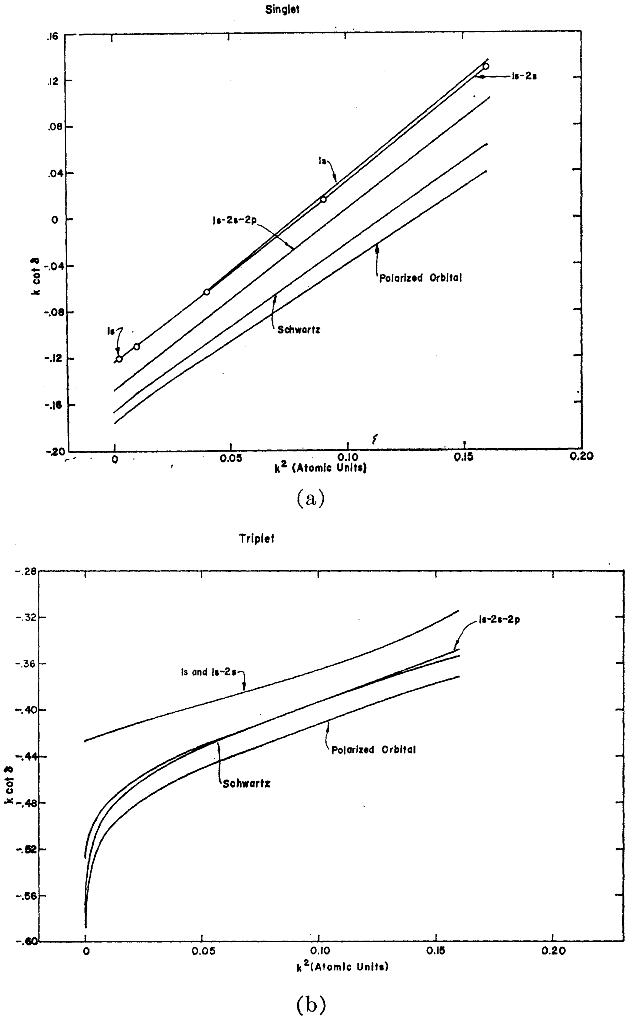
[128] R. Peterkop, Proc. Phys. Soc. (London) **77**, 1220 (1961).

defined either by Eq. (III.49) or by Eq. (III.56) and calculated in different approximations, are listed in Table XI. Probably the best values are those of Schwartz,[93] who used a Kohn variational method with up to fifty trial functions of the type given by Eqs. (V.17) and (V.18), with appropriate modifications to allow more naturally for the dipole polarization of the hydrogen atom.

These results support the conclusions of the positron results. Namely, the induced dipole polarization potential is the most significant physical phenomenon involved in very low energy atomic scattering and the eigenfunction expansion converges too slowly to yield reliable values for the scattering. It cannot be stressed enough that these statements owe their importance to the existence of the recently established rigorous extrema principles.

In order to give a somewhat more detailed appraisal of the results collected in Table XI, it is necessary to correlate the principal features of the different approximations. To begin with, if we consider only the spherically symmetric part of the total S-wave equation [i.e., setting $l_1 = 0$ in Eq. (VI.7)] then the $1S$, $1S$-$2S$, and Temkin's δ_0 results are in reasonably close agreement for both spin states. The results of such approximations differ markedly from those obtained by Temkin[106] (Legendre polynomial expansion of the S-wave function) and Schwartz[93] (variational approach using the Hamiltonian in its nonseparable form), which are in substantial agreement with each other. Lying between these two sets of results are those calculations[64,101] which make some allowance for the dipole polarizability by including the $2P$ state of hydrogen. This is to be expected, since, as pointed out in Sec. III (a), only 65.77% of the induced polarization potential is included in these approximations.

In Table XI we include the result of an interesting calculation carried out by Ohmura and Ohmura,[129] who used the Pekeris[130] H^- ion 161- and 203-parameter wave functions together with an effective range expansion [given by Eq. (III.45)], about the H^- ion bound state, to predict a value for the singlet scattering length. Although the use of (III.45), rather than (III.56), is not strictly justified, it turns out that the nonlinear terms in (III.56) are sufficiently small, owing to the relatively large value of the singlet scattering length, not to introduce much error into this calculation.



(a)

(b)

FIG. 12. Effective range plots for the singlet and triplet S-phase shifts for several calculations: $1s$,[46] $1s$ - $2s$,[54] $1s$ - $2s$ - $2p$,[64] Schwartz,[93] polarized orbital.[103]

Plots of $k \cot \delta$ against k^2 for the singlet and triplet states are drawn in Figs. 12(a), and 12(b), respectively. The singlet results all show nearly linear behavior for small k^2, which implies that the nonlinear terms in Eq. (III.56) are not important in this spin state. These results can be used to justify the assumption of Ohmura *et al.*[129] using Eq. (III.45). On the other hand, the triplet results show strong evidence of large nonlinear terms in the effective range expansion when the induced dipole polarization potential is taken into account. These nonlinear terms are seen to be significant only for $k^2 \lesssim 0.03$. Above this energy, we see that the eigenfunction expansion results of Burke and Schey[64] agree with the triplet results of Schwartz,[93] which restores some confidence in the eigenfunction approach away from the elastic

---

[129] Y. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960); see also T. Ohmura, Y. Hara, and T. Yamanouchi, Prog. Theoret, Phys. (Kyoto) **22**, 152 (1959), **20**, 82 (1958); Phys. Rev. **121**, 2 (1961).

[130] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

scattering threshold. However, in Fig. 12(a), we see that the results of the above two calculations actually diverge slightly as k^2 increases! A possible explanation of this "breakdown" of the eigenfunction approach may be due to neglect of the hydrogen ion.

We concur with Gerjuoy[131] in his assertion that the most important advance in atomic collision theory in recent years has been the development of methods for obtaining bounds, due mainly to Spruch and his collaborators although others[77,85,132] have made contributions.

In conclusion, we note that no experimental results have been reported, to date, at sufficiently low energies to make direct comparison with the above electron or positron scattering length calculations.

(b) Elastic Scattering: Electrons

The low-energy elastic scattering of electrons by hydrogen atoms has been the subject of the most detailed theoretical and experimental investigation of any of the processes considered here. Unfortunately, for nonzero incident energies, we no longer have at our disposal rigorous mathematical criteria for deciding which is the best theoretical result. In the absence of rigorous extrema principles for the elements of the $\mathfrak{R}$ matrix, our attempt to evaluate both the merits of the various theoretical methods and the accuracy of the experiments will be somewhat inconclusive. Nevertheless, we hope that certain guiding principles for the different approximations will be discovered.

Most of the theoretical methods used on this problem have been discussed in Secs. IV–VI. The most accurate results for $L = 0$, over the energy range $0 < k^2 < 0.75$, are probably the results of Schwartz,[93] and Temkin.[106] In Fig. 13 we compare the singlet S-wave phase shifts calculated in several approximations.

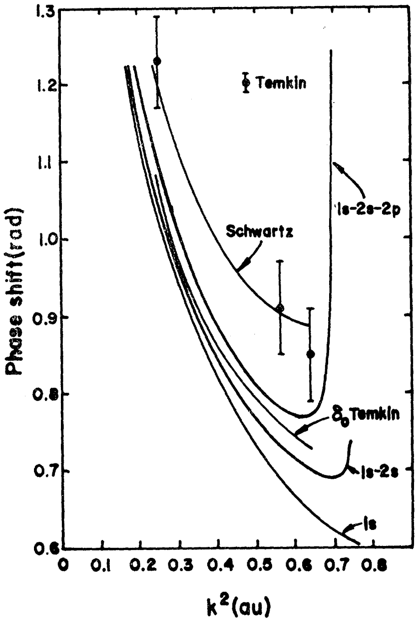


FIG. 13. S-wave phase shifts calculated in the $1s$,[46] $1s$ - $2s$,[57] $1s$ - $2s$ - $2p$[64] approximations, and by Schwartz[93] and Temkin.[106]

Assuming that Schwartz' results are correct, then we see that including virtual excitation to the $2S$ and $2P$ states only, allows for about one half of the short range correlation force effective in this spin state. The triplet $L = 0$ phase shifts for the different approximations agree quite well.

In Table VII we give the results of including further bound hydrogen states in the eigenfunction expansions for $L = 0$ (singlet). It is seen that the phase shift is hardly improved and we believe that the hydrogen ion and/or continuum hydrogen states must be included to obtain the correct result. We conclude that in those states where correlation effects are strong the close-coupling approximation including only bound states is liable to be up to ten percent in error.

In the $L = 0$ singlet state the $1s$-$2s$-$2p$ approximation phase shift appears to resonate above $k^2 = 0.7$. Unfortunately, in this energy region neither Schwartz nor Temkin has evaluated phase shifts. Burke and Schey[64] have analyzed this resonance and found its position at 9.61 eV and its full width as 0.109 eV. This resonance appears to arise at a slightly higher energy in the $1s$-$2s$ approximation.[57] Further resonances appear to exist in the $1s$-$2s$-$2p$ approximation for higher angular momenta, see Fig. 14. These also lie near the second quantum-level threshold. It is a very interesting question to decide whether these resonances exist in nature, or are a manifestation of the close-coupling approximation.

The P-phase shifts calculated by various approximations are shown in Fig. 14. The long-range polarization potential α/r^4 plays a larger role away from threshold here than in the S states. It seems probable, however, that it is still the short range correlation in the singlet P state that causes most of the error in the $1s$-state exchange approximation. The triplet phase shift, which gives by far the larger of the two contributions to the total cross section, is probably quite accurately given by the $1s$-$2s$-$2p$ results or the polarized orbital results.

For higher partial waves, arguments were given by Burke and Schey[64] that the α/r^4 potential domi-

---

[131] E. Gerjuoy, Revs. Modern Phys. **33**, 544 (1961).

[132] I. C. Percival, Proc. Phys. Soc. (London) A**70**, 494 (1957); Phys. Rev. **119**, 159 (1960); Proc. Phys. Soc. (London) **76**, 206 (1960); V. Risberg, Arch. Math. Naturvidenskab **53**, 1 (1956); T. Ohmura, Phys. Rev. **124**, 130 (1960).

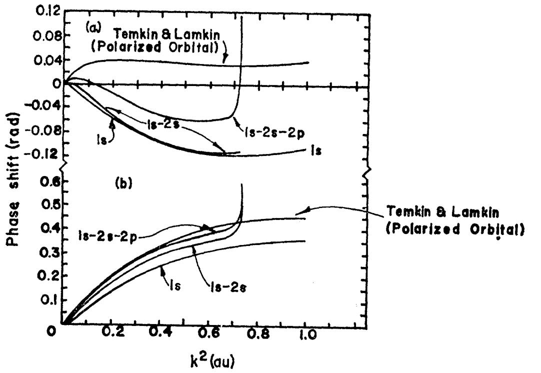


FIG. 14. P-wave phase shifts calculated in the $1s$[46], $1s$ - $2s$,[57] $1s$ - $2s$ - $2p$[64] approximations and by Temkin and Lamkin.[103] Part (a)—singlet; part (b)—triplet.

nates the scattering up to $k^2 \approx 0.5$ for the D wave and up to $k^2 \approx 0.75$ or higher for the $F, G, \cdots$ waves. In these regions the first term in the expansion

$$\tan \delta_l = [\pi\alpha/8(l+3/2)(l+1/2)(l-1/2)]k^2 + \cdots, \tag{VII.1}$$

given by O'Malley *et al.*,[41] will give a good approximation to the correct phase shift. Of course, the $1s$-$2s$-$2p$ approximation gives results for these states which are in error by a factor of 2/3 since only 2/3 of the correct α is effectively included by the $2p$ state.

In Figs. 3 and 4 we present a comparison of theory and experiment for the differential and total cross sections, respectively. The agreement for the total cross section between the two sets of experiments and the various theoretical calculations is good within the experimental errors except for the results of Bransden *et al.*[101] Here their triplet P-phase shift seems to give too large a cross section; an indication that the adiabatic method, which they used, tends to overestimate the effect of the polarization potential. The singlet S-state resonance produces a small wiggle in the $1s$-$2s$-$2p$ curve at $k^2 \approx 0.7$. The differential cross section results are also in agreement with experiment apart from an over-all normalization at the lowest energy. The difference in the P-phase shifts between the $1s$-$2s$ and the $1s$-$2s$-$2p$ results is important only at small scattering angles, where there are no experimental measurements for comparison.

In Fig. 15 the spin-flip differential cross section, predicted in the $1s$-$2s$-$2p$ close-coupling approximation,[32] is presented for four energies. The angular variation is more pronounced than for the corresponding differential cross sections, Fig. 3. Therefore, experimental measurements of this quantity may provide a more sensitive test of the corrections of the higher partial wave phase shifts.

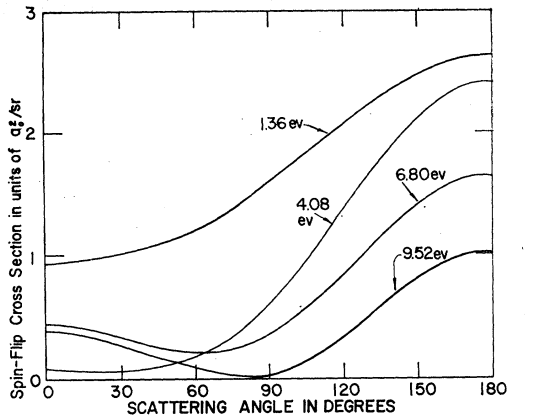


FIG. 15. Spin-flip cross section as a function of scattering angle for four incident electron energies.[32]

Finally, in Table XIII, we give the $1s$-$2s$ and the $1s$-$2s$-$2p$ approximation partial and total elastic cross sections for six energies *above* the second quantum-level excitation energy. The addition of the $2p$ state only modifies appreciably the low energy P- and D-state contributions, leaving the S-state contribution relatively unaltered. Also, as expected, the space symmetric singlet state is affected to a larger extent than the space antisymmetric triplet state. The effect on the total cross section is small. It is probable that the $1s$-$2s$-$2p$ total cross section results are accurate to within a few percent. Unfortunately, there is no experimental work in this energy region for comparison.

(c) $1s$-$2p$ Excitation: Electrons

The $1s$-$2p$ cross section has been measured by Fite and Brackmann[15] and extended to low energies by Fite, Stebbings and Brackmann.[16] Their results are presented in Fig. 5 and a description of their experiment given in Sec. II (b). Theoretical estimates of this cross section have been made using the Born approximation[123]; the distorted wave approximation for the low angular momenta, the Born-Oppenheimer approximation for the high angular momenta,[60] and the $1s$-$2s$-$2p$ close-coupling approximation for the low angular momenta with the Born approximation for the high angular momenta[66] [see Sec. VI (g)]. A comparison of experiment and theory for the experimentally measured quantity $Q_\perp$, is presented in Fig. 16. This quantity is obtained by counting photons emitted perpendicular to the electron beam and assuming an isotropic photon distribution. The agreement between experiment and theory is very poor, particularly at the lower energies $\sim$20 eV. In view of this discrepancy, it is necessary to consider in more detail the probable ranges of validity of the theoretical approximations made.

TABLE XIII. Partial wave and total elastic e^-H cross sections calculated in the 1s-2s[55, 56] and 1s-2s-2p[66] approximations for $k^2 > 0.75$. Spin weighting factors are included.

k^2	Spin State	Approximation	$L = 0$	$L = 1$	$L = 2$	$L = 3$	$L = 4$	$L = 5$	$L = 6$	Total
0.81	Singlet	1s-2s	0.436	0.046						
		1s-2s-2p	0.447	0.0098	0.047	0.005				0.509
	Triplet	1s-2s	3.687	1.377						
		1s-2s-2p	3.687	1.731	0.081	0.019				5.517
1.00	Singlet	1s-2s	0.286	0.0333	0.0014					
		1s-2s-2p	0.264	0.0101	0.0654	0.0081	0.0019	0.0006		0.350
	Triplet	1s-2s	2.895	1.157	0.057					
		1s-2s-2p	2.906	1.372	0.093	0.0168	0.0059	0.0019		4.396
1.21	Singlet	1s-2s	.186							
		1s-2s-2p	0.172	0.0133	0.0580	0.0102	0.0025	0.0009		0.256
	Triplet	1s-2s	2.297							
		1s-2s-2p	2.297	1.086	0.095	0.0160	0.0068	0.0026		3.504
1.44	Singlet	1s-2s	0.140	0.0107	0.0005					
		1s-2s-2p	0.127	0.0105	0.0351	0.0100	0.0028	0.0011	0.0005	0.187
	Triplet	1s-2s	1.829	0.815	0.068					
		1s-2s-2p	1.827	0.885	0.0938	0.0153	0.0069	0.0031	0.0014	2.832
2.25	Singlet	1s-2s	0.088	0.0012						
		1s-2s-2p	0.0836	0.0020	0.0049	0.0039	0.0022	0.0011	0.0006	0.098
	Triplet	1s-2s	0.971	0.486	0.0718					
		1s-2s-2p	0.966	0.515	0.0843	0.0143	0.0053	0.0029	0.0016	1.589
4.00	Singlet	1s-2s	0.065							
		1s-2s-2p	0.0579	0.0089	0.0014	0.0008	0.0007	0.0005	0.0004	0.071
	Triplet	1s-2s	0.412							
		1s-2s-2p	0.398	0.241	0.0631	0.0140	0.0040	0.0018	0.0011	0.724

When the $\mathcal{R}$-matrix elements calculated in the Born approximation[123] are compared with those of the 1s-2s-2p close-coupling approximation,[66] we see that the Born approximation only becomes valid (relative to the more sophisticated close-coupling approximation) at quite high angular momenta at all the energies considered. For example, for $L = 5$ and $k^2 = 1$, the $\mathcal{R}_{14}$-matrix element, which dominates the $\mathcal{R}_{13}$ element in its contribution to the 1s-2p cross section, still differs by ~15% in these two approximations. However, the total contribution to the 1s-2p cross section from this and higher angular momentum states is ~2%. For $L = 7$ and $k^2 = 4.0$ the two approximations differ by only 3%. Here, however, the total contribution to the cross section from this and higher angular momentum states is ~40 - 50%. It would seem valid, therefore, to use the Born approximation for angular momenta larger than these quoted explicitly above, but not valid to try and extend its application to lower angular momenta, particularly at the lower energies $k^2 \sim 1.0$. The question of the accuracy of the low

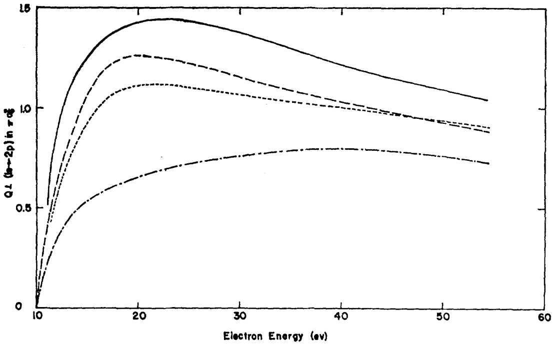


FIG. 16. Experimental and theoretical results for the cross section Q_+ (1s - 2p). Curve — · — · is experimental[16]; curve — — — was calculated using the close coupling approximation[66]; curve ··· are the distorted wave results[60]; while the full line curve was calculated using the Born approximation.

TABLE XIV. 1s-2p partial cross section contributions. BO, Born-Oppenheimer approximation; EDW, distorted wave approximation allowing for exchange (Khashaba and Massey[60]); cc, close-coupling 1s-2s-2p approximation.[66] The singlet and triplet partial cross sections contain the appropriate spin weighting factors. The values of k_2 quoted are those for the incident electron. Part a: contribution from the state with the angular momentum of the outgoing electron $l_2 = 0$, i.e., total angular momentum $L = 1$. Part b: sum of contributions from states with $l_2 = 1$, i.e., $L = 0$ and 2.

	Singlet			Triplet		
k^2	BO	EDW	CC	BO	EDW	CC
		a $l_2 = 0$, $L = 1$				
1.0	0.00575	0.0355	0.110	01.16	0.168	0.080
1.44	0.040	0.0040	0.081	0.271	0.0383	0.0416
2.25	0.030	0.00021	0.0176	0.0502	0.0091	0.0133
4.0	0.00825	0.000013	0.0024	0.0098	0.00144	0.0038
		b $l_2 = 1$, $L = 0$ and 2				
1.0	0.327	0.378	0.289	0.0067	0.0045	0.0491
1.44	0.297	0.402	0.324	0.0218	0.0167	0.0634
2.25	0.122	0.092	0.111	0.0323	0.0204	0.0463
4.0	0.0275	0.0118	0.0204	0.0210	0.0067	0.0191

TABLE XV. Cross sections in units of πa_0^2 and polarization fractions of the impact radiation for 1s-2p excitation calculated in the 1s-2s-2p close-coupling approximation.[66] The singlet and triplet partial cross sections contain the appropriate spin weighting factors. The values of k^2 quoted are those for the incident electrons.

k^2	Singlet		Triplet		Total Cross Sections				Polarization of the Impact Radiation
	$Q(\pm)$	$Q(0)$	$Q(\pm)$	$Q(0)$	$Q(\pm)$	$Q(0)$	Q	$Q_\perp$	
0.81	0.0534	0.1266	0.0149	0.0968	0.0683	0.2234	0.3599	0.3853	0.2009
1.00	0.0735	0.3011	0.0262	0.2994	0.0997	0.6005	0.7909	0.8820	0.2835
1.21	0.0913	0.4386	0.0482	0.3763	0.1395	0.8149	1.0939	1.2047	0.2799
1.44	0.0878	0.4487	0.0753	0.4052	0.1631	0.8539	1.1801	1.2934	0.2667
2.25	0.0871	0.2533	0.1373	0.3890	0.2244	0.6423	1.0911	1.1596	0.1800
4.00	0.0740	0.1160	0.1655	0.2767	0.2395	0.3927	0.8716	0.8968	0.0855

partial wave contributions in the close-coupling approximation still remains.

In Table XIV a comparison is presented between the close-coupling approximation cc, the distorted wave approximation including exchange EDW, and the Born-Oppenheimer approximation BO, for l_2 equal to 0 and 1 (l_2 is the angular momentum of the outgoing electron). In general, the agreement is better for $l_2 = 1$ than for $l_2 = 0$. It seems reasonable to assume that the agreement would be better still for $l_2 > 1$ where the distortion is smaller. In general, for those terms where the agreement between the EDW and the cc approximations is poor, their contribution to the total cross section (given in Table XV) is small. Finally, we expect the cc approximation, because it allows for the long range 2s-2p coupling and also treats the distortion more correctly, to give better results than the EDW approximation, where the two methods disagree.

The above arguments lead us to believe that the close-coupling results are the best theoretical results available to date.

We see from Fig. 16 that, as the theoretical approximations improve, the excitation cross section 1s-2p tends toward the experimental result. We have seen in Sec. VII(a) that the eigenfunction expansion approach can converge slowly, see Fig. 12(a), and Table VII. We were able to assess this slow convergence by applying extrema criteria to calculations on the scattering length. Unfortunately, no equivalent rigorous criteria are known for the multichannel problem, although some work on a related problem with cutoff potentials[99] has been reported. Therefore, we are unable to state, conclusively, that the cc results have converged to the true cross sections, and therefore the cross section should be remeasured.

In Table XV we present the close-coupling results of Burke, Schey, and Smith.[66] For $k^2 = 1.0$, 1.44, 2.25, and 4.0, the Born approximation results of Seaton *et al.*[123] for $L \geqslant 6$, 7, 7, and 8, respectively, were used to determine the total cross section. For $k^2 = 1.21$, where the Born results were not available, reasonable interpolations from neighboring k^2 and L values were used for $L = 6$ and 7. Similarly the $L = 4$ and 5 contributions for $k^2 = 0.81$, where the Born approximation is invalid, were found by interpolation. This procedure was valid at both energies since the added contribution did not amount to more than a few percent of the total cross section. A few percent correction due to contributions from $L \geqslant 14$ was also added to the $k^2 = 4.0$ result by means of an extrapolation procedure. The results given in Table XV are probably accurate, within the 1s-2s-2p approximation, to better than 1%.

$Q(\pm)$ and $Q(0)$ are the cross sections for the excitation of the $2pm_l = \pm 1$ and the $2pm_l = 0$ levels, respectively. The polarization of the impact radiation, emitted at right angles to the electron beam, is given in the last column of the table. The polarization fraction can be written[17] as

$$P = \frac{I_{\shortparallel} - I_{\perp}}{I_{\shortparallel} + I_{\perp}},$$

where $I_{\shortparallel}$ and $I_{\perp}$ are the intensities of the radiation with an electric vector parallel and perpendicular to the beam. P, at right angles to the beam, can be written in terms of $Q(\pm)$ and $Q(0)$, see Eq. (III.33). For large energies, $P \to 0$, while as $k^2 \to$ threshold ($k^2 = 0.75$), $Q(\pm)/Q(0) \to 0$ and $P \to 3/7$.

Using these results together with Eq. (II.2) we derive

$$Q_{\perp} = 0.918Q + 0.246Q(0),$$

where Q is the total 1S-2P excitation cross section.

We conclude this commentary on $Q(1S\text{-}2P)$ by remarking that Akerib and Borowitz[116] have estimated the scattering amplitude for this process. Their computed cross sections are in qualitative agreement with experiment.

(d) 1s-2s Excitation: Electrons

The total cross section for the excitation of hydrogen atoms from the ground state to the metastable $2s$ state has been computed in the $1s$-$2s$ strong-coupling approximation[55,56] and in the $1s$-$2s$-$2p$ close-coupling approximation.[65,66] Earlier work, such as the distorted wave approximation[133] and the nonexchange calculations,[45,53] will not be discussed since they provide only approximations to the results presented here.

The most remarkable feature of these results is the quite good agreement of the $1s$-$2s$ and $1s$-$2s$-$2p$ approximations both with regard to individual partial cross sections, see Table IV, and total cross sections, see Fig. 18. In particular, we note that the $2p$ state has very little effect in the triplet spin state, except close to threshold. In the singlet state, the effect of including $2p$ is to reduce slightly the cross section at higher energies and increase it near the threshold. Further we see that, in general, the highest angular momentum, where comparison is possible ($L = 3$), is modified to a larger extent than the lower angular momenta. The effect on the total cross section is, however, small from these higher angular momentum states. The above effects can be understood qualitatively as follows. Because the inclusion of the $2p$ state allows for some nonspherical distortion of the atom, then certain long range interactions are automatically included in the $1s$-$2s$-$2p$ approximation. These interactions play their largest role in the higher angular momenta states and near the threshold. Actually, using the probably correct Born results from $L = 7$ to 14 at 50 eV, accounted for 20% of the total cross section. Again we expect that distortion of the atomic wave functions, partially allowed for by the inclusion of the $2p$ state, to be of greater importance in the singlet (space symmetric) where the electrons can approach closer together than in the triplet state.

This cross section has also been computed by Akerib and Borowitz[116] but their results do not agree even qualitatively with those of Fig. 18. In particular, the impulse approximation predicts a broad maximum in the total cross section vs energy curve around 60 eV compared with a narrow maximum around 14 eV predicted by the eigenfunction expansion methods and experiment. Furthermore, the magnitude of the maximum is considerably below experimental and other theoretical results. In view of the reasonable success of the impulse approximation in calculating $Q(1s\text{-}2p)$, see the previous subsection, and the ionization cross section, its failure here is somewhat surprising.

We see from Fig. 18 that the $1s$-$2s$-$2p$ results agree better with the Born approximation than the second Born.[124]

As remarked in Sec. II(b) and illustrated by Figs. 6 and 7, the two experimental measurements by Lichten and Schultz[18] and by Stebbings *et al.*[20] are in poor absolute agreement. From an experimental point of view, the normalization procedure adopted by Stebbings *et al.* seems to be preferred, although there does exist the possibility that errors may be overlooked by normalizing too far from the region of interest. If we renormalize the results of Lichten and Schultz to have the same maximum value as Stebbings *et al.* at about 13 eV (which is allowed by their quoted experimental errors), then the shape of the two curves agree very well.[62] However, it is of great importance for as accurate as possible a theoretical estimate to be made of this cross section in order to throw further light on this normalization problem, as well as to provide criteria for the goodness of various approximations.

Direct comparison with experiment is made difficult by the fact that the $2s$ state is also populated by electromagnetic transitions from the higher atomic states which are also excited in the collision. Assuming that the $3p$ state gives the largest contribution, we can write the production of metastable H by all atomic processes[134] as

$$\sigma_p(2s) = \sigma_T(2s) + 0.21\sigma(3p)$$

where $\sigma_T(2s)$ corresponds to the theoretically calculated quantity $Q(1s\text{-}2s)$. Both sets of experimental results are corrected using for $\sigma(3p)$ the experimental results of Fite *et al.*[16] for $\sigma(2p)$ renormalized at high energies to the Born $\sigma(3p)$. We present the comparison of theory and experiment in Fig. 18. In Table VIII we present some preliminary calculations on $Q(1s\text{-}3p)$ in the strong-coupling approximation; we compare these results with Lichten's estimate in Fig. 17. The total cross section at 50 eV, for $L \leqslant 4$ is 0.04 πa_0^2 which is only 1/5 of the Born value.[2] However, the strong-coupling results had not converged and it seems likely that very high L values will be required. This point is currently being investigated.[66]

It is difficult to understand how the theory can be made to agree with the experimental results of Stebbings *et al.* Unfortunately, in the absence of rigorous extrema criteria we have no way of assessing objectively the error incurred in the calculations. However, another piece of experimental information is available; namely, the exchange cross section as measured

---

[133] G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) A**212**, 521 (1952).

[134] H. A. Bethe, *Handbuch der Physik*, edited by Geiger and Scheel (Verlag Julius Springer, Berlin, 1933), Vol. **24**, pt. 1, p. 508.

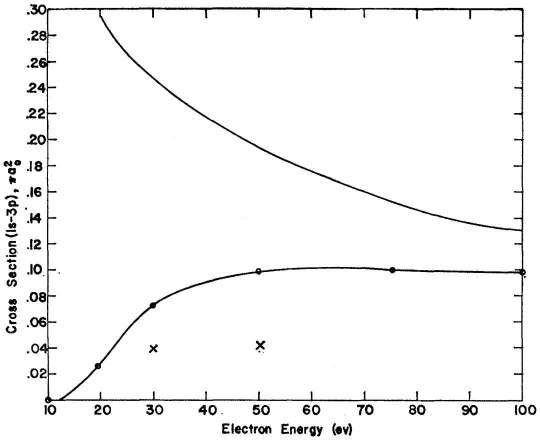


FIG. 17. e^{-}H excitation cross section $1s$ - $3p$. Dots—Born approximation;[2] crosses—strong-coupling approximation;[66] open circles—experimental[16] Q ($1s$ - $2p$) normalized to the Born values for $1s$ - $3p$.

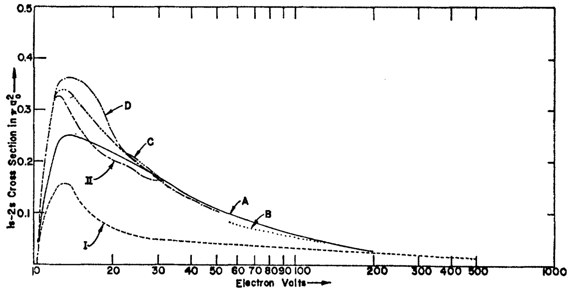


FIG. 18. Electron-hydrogen atom excitation cross section $1s$ - $2s$. Curves I and II are the experimental results of Stebbings *et al.*[20,21] and of Lichten and Schultz,[18] respectively. The theoretical curves were calculated as follows: A–Born approximation; B–second Born approximation;[124] C–$1s$ - $2s$ strong-coupling approximation;[56] D–$1s$ - $2s$ - $2p$ approximation.[66]

by Lichten and Schultz. This cross section is one-half the spin-flip cross section, $|A_t - A_s|^2/4$, where A_s and A_t are defined in Eq. (III.26). Burke *et al.*[66] have computed this quantity and at $k^2 = 1.0$, they obtain that this cross section is 0.11 πa_0^2 which agrees very well with the result quoted by Lichten and Schultz.

(e) Ionization

Calculations of the ionization cross section have been of an exploratory nature only. Indeed, the total cross section has been computed only in the Born approximation[126] and Impulse approximation,[116] see Fig. 10.

Close to threshold, i.e., $k_1^2 = 1$, Geltman[127] has developed a modified form of the Born approximation and shown that the total ionization cross section depends linearly on the *excess* incident energy. This result has also been obtained by Akerib and Borowitz.[116] However, Wannier[135] has derived a threshold law for single ionization which has the form $\mathcal{E}^{1.127}$, where $\mathcal{E}$ is the excess incident energy. Wannier's result was obtained by an approximate solution of the classical three-body problem, coupled with statistical mechanical arguments. Massey[2] (p. 372) has pointed out that Wannier's result is in conflict with experiments on helium, which predict a linear dependence on $\mathcal{E}$.

We see in Fig. 10 that the various experimental determinations of this cross section differ most in the energy region of interest here. In particular, the results of Rothe *et al.*[24] lie about 25% (i.e., 0.2 πa_0^2) below those of Fite and Brackmann[22] at 100 eV, the latter being in reasonable agreement with the calculated values of the Impulse approximation. In view of the general failure of this approximation to predict the location and magnitude of the excitation cross sections $1s$-$2s$ and $1s$-$2p$, it is not possible to say which experimental result is supported by this calculation.

The need for additional absolute measurements at energies below 100 eV and for more accurate calculations is apparent. As remarked in Sec. VI(g), Geltman's method[127] could probably be developed in conjunction with the close-coupling approximation, Sec. IV(c).

(f) Inelastic Scattering of Positrons

Cross sections for the excitation of hydrogen atoms from the ground state level $1S$ to the $2S$ and $2P$ levels have been calculated in the strong-coupling[45] and close-coupling[66] approximations. The partial wave cross sections are given in Table V. Where comparison is possible, except for $Q(2S\text{-}2S)$ at $l = 0$, the two sets of results agree reasonably well, the agreement improving with increasing energy and L. A tentative conclusion indicated by these results is that the eigenfunction expansion converges very quickly. However, it is recalled that the effect of virtual positronium formation was of major importance at the elastic threshold. It is conceivable, therefore, that the results of calculations which include real positronium formation might be appreciably different from those given in Table V. Such calculations are now being performed,[136] and will yield the cross sections for positronium formation into the $1S$ and $2S$ states.

At the present time, the only calculations reported for the cross section for positronium formation are those of Massey and Mohr[137] and are reproduced in

---

[135] G. H. Wannier, Phys. Rev. 90, 817 (1953).

[136] W. J. Cody (private communication).

[137] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc. (London) A67, 695 (1954).

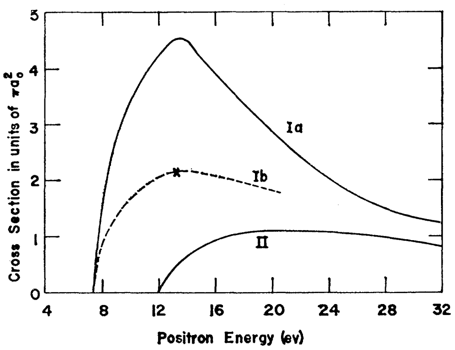


FIG. 19. Cross sections for capture of electrons from hydrogen atoms by positrons. Ia and Ib are the Born approximation and distorted positron wave approximation, respectively, for capture into the 1s state of positronium; II—capture into the 2s state, multiplied by 5.

Fig. 19. These calculations were carried out in the Born approximation.

VIII. CONCLUSIONS

The rigorous extrema principles at zero incident energy are of crucial importance since they provide the first mathematical criteria for deciding which is the better of two approximations. Applying these principles, we have seen that the eigenfunction-expansion approach converges very slowly near to the elastic threshold. We have pointed out that a calculation which took H^- into account might help the convergence considerably. In any case, such a calculation is desirable in order to get a bound on the scattering length. These principles have established the dominant role played by the induced dipole polarization potential at $k^2 \approx 0$. This fact corroborates Wigner's observation[138] that long range forces determine the nature of the scattering parameters at thresholds.

The absence of extrema criteria away from $k^2 = 0$ make it impossible to assess, definitively, the merits of theoretical approximations and experiment. One would hope that if one expanded about the *inelastic* thresholds in the effective range theory then it might be possible to define analogous quantities to the scattering length. Rigorous bounds on such quantities would certainly help in clarifying the disagreement which exists between theory and experiment for the inelastic cross sections.[139] From experience gained at the elastic threshold, it is desirable to isolate the long range interactions at the inelastic thresholds.

The narrow resonances in the total e^-H cross section[64] pose an interesting problem. Massey[140] has investigated the formation of such resonances within the framework of the strong-coupling approximation. Since $k_2^2 < 0$, in the energy region where the resonances appear, the second equation in (IV.6) resembles an eigenvalue problem. Massey has neglected the inhomogeneity in this second equation and solved the eigenvalue problem for a variety of potentials. He has used his derived eigenvalue k_2^{ε}, and eigenfunctions to generate resonances in the scattering functions F_1. The possibility that these resonances are mere anomalies in the 1s-2s-2p approximation rather than physical states cannot be overlooked. Indeed, evidence that this might be the case is furnished by the approximation itself. In the no-exchange approximation, there appears an $L = 1$ resonance at $k^2 \approx 0.225$ which does not appear in either the singlet or triplet phase shifts. Such peculiar results are not uncommon in the eigenfunction-expansion method. Smith and Burke[54] observed a pronounced minimum in the elastic scattering cross section in the 1s-2s approximation, neglecting exchange. Nevertheless, further theoretical work is required before discarding their possible existence.

The disagreement between theory and the Born normalized experimental measurements for the excitation cross sections pose a problem which should be resolved. An absolute measurement of $Q(2S)$, below $k^2 = 8/9$ in order to avoid complications from the cascade processes, accurate to about 0.01 πa_0^2, would definitely tell us whether or not the eigenfunction-expansion approach can be used to compute excitation cross sections. However, as indicated by Smith *et al.*[45] and corroborated by later work[66,59] the partial-wave approach converges extremely slowly for successive L values. Because of this slow convergence, it is certainly worthwhile to examine carefully those theoretical proposals which avoid the partial-wave expansion.

ACKNOWLEDGMENTS

The authors would like to thank Dr. H. M. Schey and Valerie M. Burke for helpful discussions. They are grateful to Dr. Schey for permission to present the results of the 1s-2s-2p approximation, above threshold, prior to their publication. They are indebted to S. F. Mendicino, D. F. Jordan, and S. Zawadzki for their help with the various computer programs. Finally, they would like to express their gratitude to Dr. W. L. Fite for helpful correspondence and Dr. P. A. Fraser and Dr. R. P. McEachran for their comments on the manuscript.

---

[138] E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[139] See for example, R. G. Newton, Ann. Phys. (N. Y.) **4**, 29 (1958); M. Ross and G. L. Shaw, *ibid.* **13**, 147 (1961); Phys. Rev. (to be published).

[140] H. S. W. Massey (private communication).