UCRL-10878

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

A GENERALIZED OPTICAL-POTENTIAL METHOD AND ITS APPLICATION TO THE SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Research and Development

UCRL-10878
UC-34 Physics
TID 4500 (19th Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

A GENERALIZED OPTICAL-POTENTIAL METHOD AND ITS APPLICATION TO THE SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN

Robert Ta-Pang Pu

(Thesis)

June 18, 1963

Printed in USA. Price $1.75. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

A GENERALIZED OPTICAL-POTENTIAL METHOD AND ITS APPLICATION TO THE SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN

Contents

Abstract v

I. Introduction

A. General Remarks 1

B. Physical Picture 2

C. Outline 4

II. Two Conventional Methods 5

A. Eigenfunction-Expansion Method 5

B. Optical-Potential Method 11

III. Formal Derivation of the Generalized Optical-Potential Method 14

A. Derivation Without the Pauli Principle 14

B. Modification for Electron-Hydrogen-Atom Scattering 18

IV. Numerical Results and Discussion 26

A. S-Wave (L=0) Phase Shifts 26

B. P-Wave (L=1) Phase Shifts 36

C. D-Wave (L=2) Phase Shifts 38

D. F-Wave (L=3) and Higher-Order Phase Shifts 38

E. Comparison with Experiment 40

V. Conclusion 43

Acknowledgments 55

Appendices

A. Proof That a^+ and Π_N Commute 56

B. Reduction of the Partial-Wave Treatment to Radial Equations 56

C. Numerical Procedure for Solving the Set of Coupled Integral-Differential Equations 59

D. Proof of Relaxation of Restriction on ϕ's in Eq. (3B-16) 62

E. The Algebraic Problem of the Modified Trial Wave Function, Eq. (E-1) 65

F. Calculation of the First-Order Nonadiabatic Correction of the Optical-Potential for Electron-Hydrogen Scattering 67

References 70

A GENERALIZED OPTICAL-POTENTIAL METHOD AND ITS APPLICATION TO THE SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN

Robert Ta-Pang Pu

Lawrence Radiation Laboratory
University of California
Berkeley, California

June 18, 1963

ABSTRACT

A generalized optical-model-potential method for calculation of the scattering of charged particles by atoms is described. The method is shown to combine, in practical applications, the advantages of two conventional approaches, the eigenfunction expansion method and the optical-potential method, and to contain these two approaches as limiting cases. With certain modification to allow for the Pauli exclusion principle explicitly, the method is applied to the elastic scattering of electrons by hydrogen atoms for energies below the excitation of the second quantum level (10.2 eV), with 1s, 2s, 2p hydrogen atomic states used in the close-coupling scheme. The resulting coupled set of integro-differential equations, with appropriately approximated generalized optical potentials, was integrated numerically on an IBM 7090 computer, yielding phase shifts in various total spin and total angular momentum states.

Results from this calculation are compared with other theoretical predictions and available experimental data. The short-range interelectron correlation effect is found to be of major importance for S-wave scattering in the entire energy range except very near zero energy. The influences of the long-range polarization potential and the short-range effect become comparable for P-waves. For D-waves, the long-range polarization potential begins to assume a major role in the scattering, and for F and higher waves it becomes singularly dominant throughout.

Extremely narrow resonance-type effects in phase shifts of various spin and angular momentum states are found at energies slightly below the second quantum level. The resonance in singlet S-state is analyzed in detail, by a Breit-Wigner type fit, and is found to be centered at 9.51 eV with a narrow full width of 0.067 eV. For the scattering length of singlet S-wave, a value of 6.520 (in unit of Bohr radius) is obtained.

The method is less successful in singlet low-angular-momentum waves where short-range correlation effect is important. A modified trial wave-function form is suggested for these cases, to take better account of the mutual repulsion between electrons.

I. INTRODUCTION

A. General Remarks

The problem of the scattering of a charged particle by an atom (henceforth referred to simply as atomic scattering) has been of continued interest to physicists since the advent of quantum mechanics. For purely theoretical interest, it has been used both as a tool for probing the atomic structure and in turn as a test of the validity of nonrelativistic quantum mechanics. For practical applications, an understanding of the atomic-scattering process is of great importance in such areas as gaseous electronics, astrophysics, and, more recently, in the area of controlled thermonuclear reactions.

At high energies, the first Born approximation has been known to yield predictions in general agreement with experiments.[1, 2] On the other hand, for low-energy scattering both theoretical calculations and experimental results have been quite inadequate. Here by low-energy we mean the relative velocity of the charged particle and the target atom is of the order of that of atomic orbital electrons, or less.[3]

The experimental difficulty lies in the fact that most atoms are not monatomic at room temperature. The molecules of these elements must first be dissociated. The dissociation is invariably accompanied by the formation of excited states of the atom and free electrons, as well as ions — whose presence makes the experimental results very difficult to interpret. This is the reason that for many years most experiments were limited to monatomic noble gases only. The solution to the difficulty mentioned above was found in the use of modulated-beam techniques.[4, 5] This new technique makes possible more refined experimental results.

On the theoretical side, the difficulty lies not in principle. We know that the particles interact with Coulomb forces and that the scattering process obeys the nonrelativistic Schrödinger equation with known boundary conditions. Formal solutions can be given quite readily. However, the inherent complexity of this many-body

problem limits practical calculations to very crude approximations. More unfortunately, various approximations often yield vastly different predictions. With the lack of experimental comparison, it is difficult to assess the merits of various approximations.

Just as the modulated-beam techniques have aided the experimentalist, the recent development of high-speed electronic computers enables theorists, for the first time, to do calculations on a much larger and more ambitious scale, and to make better, though still quite limited, approximations. With better experimental results within sight, we are justified in using our best available means in theoretical calculations, to make systematic appraisals of different approximations, to assess their range of validity, and to understand better the prime mechanisms involved in low-energy atomic-scattering processes.

B. Physical Picture

It is important to have a general classical picture of the low-energy atomic-scattering process. This physical picture will aid our understanding of the theoretical methods and their various approximations which we shall mention later.

Let us assume the atom is in its initial state while the charged particle comes from infinity. As the impinging particle approaches, the electron cloud of the atom will be appreciably distorted by the field of the charged particle. If the relative velocity between the particle and the atom is rather small, we could reasonably assume that the atomic electrons will be able to follow the instantaneous motion of the incoming particle and distort adiabatically as a function of the incoming-particle position. The charged particle in turn sees an average field of this adiabatically distorted atom, which in our classical picture would be ellipsoid-shaped. Thus, at large distance, only the induced dipole polarization is important; the attractive field experienced by the particle is simply $[-(\alpha/2)/r^4]$, where α is the usual polarizability of the atom, and r is the distance between the particle and the atom. Of course, when the particle gets closer to

the atom, higher multipole fields must be included. This is the general idea behind the so-called adiabatic theory of low-energy scattering.[6, 7]

However, the incoming particle will acquire more velocity in this induced attractive field as it gets near the atom, and may attain speed comparable to that of the atomic electrons. Then the atomic electrons may not be able to distort adiabatically. The field as seen by the charged particle will not be a simple function of its position alone as described before, but will be a complicated and, in general, a velocity-dependent (i.e., nonlocal) field.

The region where the breakdown of the adiabatic condition begins depends of course on the magnitude of the induced attractive field and the incoming particle's mass and initial velocity. For lighter particles such as electrons, this effect may occur and become important before the particle reaches the target atom; we call this a long-range nonadiabatic effect. It must be kept in mind that this kind of division of the scattering process into various effects are not at all clear-cut and only roughly defined for the convenience of discussion. No effect can be completely isolated from the others.

As the particle gets very near or inside the atom, the picture of an ellipsoidal atom must be abandoned and replaced, assuming the particle to be negatively charged, by the picture of a more complicated distorted atomic electron cloud with a "bubble" moving through it. That is, the incoming particle repels the atomic electrons and creates a Coulomb hole (the "bubble") around it. Furthermore, we can no longer assume the particle sees an <u>average</u> field of the atom. The short-range correlation between the charged particle and the atomic electrons in this region may have an important effect on the scattering process. Finally, if the particle is an electron, one must properly incorporate the Pauli exclusion principle to take into account the indistinguishability of electrons. That this is a very important effect in low-energy scatterings was first demonstrated by Morse and Allis.[8]

In summary, the theoretical problem for low-energy atomic scattering is that of making adequate allowances for the physical effects mentioned above; namely, the adiabatically induced long-range polarization force, the nonadiabatic behavior and short-range interparticle correlations, and the Pauli exclusion principle–if the incoming particle is an electron. Since various theoretical approximations, in effect, place different emphasis on these physical effects, comparison with experimental results will shed light on the relative importance of these effects on the scattering. We shall always keep this in mind, and discussions in subsequent sections will be so oriented.

C. Outline

Here we give a brief outline of the general development in this work. In Sec. II, two general theoretical approaches commonly used in atomic scattering problems, the eigenfunction expansion method and the optical-potential method, are described. This leads naturally to Sec. III where we formally derive the generalized optical-potential method. Its connection with the two general methods in Sec. II and its clear advantage over both will be shown. The method is applied to the case of electron-hydrogen atom scattering. The Pauli exclusion principle requires certain modifications in the formalism, which is done in Sec. III-B. The optical potentials used in the calculation are also presented there.

Phase shifts were obtained for elastic scattering at energies below excitation threshold, and they are presented and analyzed in Sec. IV; comparisons with other theoretical calculations and available experimental results are also made. Finally, in Sec. V, some conclusions are drawn on the basis of our results, with regard to the scattering process and the theoretical methods that are used. In addition, a modified expansion form for the singlet wave function is suggested.

II. TWO CONVENTIONAL METHODS

In the treatment of atomic-collision problems, various theoretical methods, heuristic and formal, have been used. The Born expansion approach,[1] for example, is well known and often used, but is is found to be rather unsuitable for low-energy scatterings. We also have the variational method, whose brute-force-type approach has been proven to be very powerful in certain cases.[9] However, the method seems to be esthetically less appealing in that the physical picture of the scattering process becomes rather obscure.

In this section we review two formal approaches, the eigenfunction expansion method and the optical-potential method. The presentation and the associated discussions of these two methods lead naturally to the main theoretical development of this work, the generalized optical-potential method. The pertinent quantities and terms introduced in this section will also be used throughout the work.

A. Eigenfunction Expansion Method

The most widely used approach in the atomic-scattering problem is the eigenfunction expansion method. Its various subsequent approximations represent the major research efforts in this field.[1, 2] The method is characterized by the expansion of the total wave function ψ for the scattering process as a sum of the product of two uncorrelated (separable) wave functions, the eigenfunction of the atom $\Phi(z)$ and the incoming-particle wave function $\phi(x)$. The total wave function is written

$$\psi(x, z) = \left(\sum_n + \int \right) \phi_n(x)\ \Phi_n(z), \tag{2A-1}$$

where x represents the coordinates (space and spin) of the scattered particle, and z represents all the coordinates of the atom. The above expansion involves no approximations and the sum, as indicated, is over the complete discrete spectrum as well as the continuum of the unperturbed atomic wave function $\Phi_n(z)$,

$$H_A\ \Phi_n(z) = \epsilon_n\ \Phi_n(z), \tag{2A-2}$$

where H_A is the Hamiltonian of the undisturbed atom, and ϵ_n is the eigenenergy of the atom in the nth state. Since the states $\Phi_n(z)$ span the whole space of z, $\phi_n(x)$ can also be viewed as the expansion coefficient of $\psi(x, z)$.

Let K be the kinetic-energy operator of the incoming particle and V its total (Coulomb) interaction with the nucleus and the atomic electrons:

$$V = V_N + \sum_i V(\underset{\sim}{x} - \underset{\sim}{z}_i). \tag{2A-3}$$

The total wave function ψ satisfies the nonrelativistic Schrödinger equation

$$(H_A + K + V - E)\psi(x, z) = 0. \tag{2A-4}$$

The quantity E represents the total energy of the system. If the atom is in the initial state Φ_0, and the incoming particle of mass m has an initial momentum p_0, then we have

$$E = \epsilon_0 + \frac{p_0^2}{2m} = \epsilon_0 + E_0.$$

The asymptotic boundary condition is quite simple in this approach. For an incoming plane wave p_0 we have

$$\lim_{x \to \infty} \psi^{(+)}(x, z) = \sum_n{}' \left[e^{i\underset{\sim}{p}_0 \cdot \underset{\sim}{x}/\hbar} \delta_{n0} + f_n^{(+)}(\hat{x}, \hat{p}_n) \frac{e^{ip_n x/\hbar}}{|x|} \right] \Phi_n(z). \tag{2A-5}$$

The prime limits the sum to energetically open channels only, and $p_n = [2m(E - \epsilon_n)]^{1/2}$. The transition amplitude to the nth channel $f_n^{(+)}(\hat{x}, \hat{p}_n)$ is related to the transition cross section simply by

$$\sigma_n(\hat{x}, \hat{p}_n) = \frac{|p_n|}{|p_0|} \left| f_n^{(+)}(\hat{x}, \hat{p}_n) \right|^2 . \tag{2A-6}$$

Substituting the form of $\psi(x, z)$ of Eq. (2A-1) into Eq. (2A-4), multiplying on the left by various atomic wave functions $\Phi_n^*(z)$, then integrating over atomic coordinates z, we obtain an infinite set of coupled differential equations for $\phi_n(x)$:

$$\left[E_n - K\right] \phi_n(x) = \left(\sum_m + \int\right) V_{nm}\, \phi_m(x) \tag{2A-7}$$

for $n = 1 \cdots \infty$, and

$$E_n = E - \epsilon_n,$$

$$V_{nm} = \int dz\, \Phi_n^*(z)\, V(x, z)\, \Phi_m(z). \tag{2A-8}$$

Equation (2A-7) can also be variationally derived by substituting the expression of ψ in Eq. (2A-1) into

$$\delta\left[\int \psi^* (H_0 + V - E)\, \psi\, dz\right] = 0. \tag{2A-9}$$

A few remarks on this approach are in order here. Because of the product-type expansion form, the asymptotic boundary conditions of the problem are unambiguously defined. The relation for the asymptotic ϕ_0 and the transition rate is particularly simple [Eqs. (2A-5) and (2A-6)], making this approach the most convenient way of calculating reaction processes. However, the continuum part of the atomic wave function Φ in the expansion of ψ is extremely difficult to handle mathematically, and has never been included this way in practice. Recently, Rotenberg[9A] suggested use of an alternative eigenfunction-expansion basis, the Sturmian functions. These Sturmian functions are closely related to the original Schrödinger wave functions but, independent of potentials between the particles, they form a complete set without a continuum in the region of physical interest. In this sense the contribution of the usual atomic-continuum states can be included. While this indeed is a definite advantage, the fact that only one state in the Sturmian functions is a real physical wave function

seems to limit the method's practical usefulness to the elastic-scattering case only.

In subsequent sections we shall assume the incoming particle is not an electron unless specifically identified as such. This is to facilitate our general discussions. Of course when the incoming particle is an electron we must explicitly antisymmetrize the trial wave function, and introduce exchange terms and other well-known complications.[1, 3]

We now go on to the various approximations of this approach. The so-called closely-coupled-states approximation assumes that the potential matrix elements V_{nm} are zero except those between certain selected atomic states Φ_n for $n = 1, \cdots, N$. Equation (2A-7) reduces to a finite set of N coupled equations:

$$\left[E_n - K\right] \phi_n = \sum_{m=1}^{N} V_{nm} \phi_m, \tag{2A-10}$$

for $n = 1, \cdots, N$.

The same result can also be obtained by truncating the trial solution,

$$\psi_T = \sum_{n}^{N} \phi_n(x)\, \Phi_n(z) \tag{2A-11}$$

and substituting into the variational expressions Eq. (2A-9).

The choice of the closely coupled states N depends on the problem at hand. For a particular reaction process from initial atomic state Φ_0 to final atomic state Φ_n, we may close-couple just those two states and neglect all others. The resulting equations become

$$\left.\begin{aligned} \left[E_0 - K - V_{00}\right] \phi_0 &= V_{0n}\, \phi_n \\ \left[E_n - K - V_{nn}\right] \phi_n &= V_{n0}\, \phi_0 \end{aligned}\right\} . \tag{2A-12}$$

We may also include other atomic states in the close-coupling scheme, such as the degenerate states of the initial and the final atomic states, but the labor in solving the coupled equations increases tremendously with the number N.

The physical meaning of the close-coupling scheme is clear from the separable-type trial wave function [Eq. (2A-10)]. For a given incident-particle position, the total wave function becomes a linear combination of those close-coupled atomic wave functions with coefficients determined by the values of their respective incoming-particle wave functions at that point. In this sense the close-coupling scheme means we are limiting the atom to distort only within these close-coupled atomic states. Thus a close-coupling scheme with atomic s states will only provide radial, or spherically symmetric "shell" type, distortion. For nonspherical distortions such as those giving rise to the long-range dipole polarization potential, we must include atomic p states in the scheme to simulate an ellipsoidal atom.

A further approximation to Eq. (2A-12) is the omission of the term on the right in the first equation:

$$\left.\begin{aligned} \left[E_0 - K - V_{00}\right] \phi_0 &= 0 \\ \left[E_n - K - V_{nn}\right] \phi_n &= V_{n0}\, \phi_0 \end{aligned}\right\} . \qquad \text{(2A-13)}$$

This is called the distorted wave approximation: the incident particle coming in the <u>static</u> field of the atom in the initial state Φ_0, making <u>one</u> interaction and exciting the atom into state Φ_n, and finally leaving in the <u>static</u> field of the final atomic state. The elastic-scattering solution involves the first equation of Eq. (2A-13) only, and is called, appropriately, the static approximation.

We mention in passing here an even cruder approximation for Eq. (2A-13). Letting $V_{00} = 0$ and $V_{nn} = 0$, we have $\phi_0 = \exp(i\underset{\sim}{k}_0 \cdot \underset{\sim}{x})$, and the second equation of (2A-13) becomes

$$(E_n - K)\, \phi_n - V_{n0} \exp(i\underset{\sim}{k}_0 \cdot \underset{\sim}{x}). \qquad \text{(2A-14)}$$

The solution of Eq. (2A-14) can be easily obtained and it yields the transition amplitude to atomic state n:

$$f_{0n}(\underset{\sim}{k}_0, \underset{\sim}{k}_n) = -\frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right) V_{n0} \exp[i(\underset{\sim}{k}_0 - \underset{\sim}{k}_n)\cdot \underset{\sim}{x}]\, dx \,, \qquad (2A\text{-}15)$$

which is just the familiar first Born approximation.

The complexity of the calculational task in solving these equations is enormous and perhaps not too apparent from the above presentation. We note that, up to the present, the majority of work on low-energy atomic scatterings has been limited to the distorted-wave approximation or even the static approximation.[1, 3] The most ambitious work has been on the close-coupling calculation of two or three states.[3]

Besides being the most general and, in particular, the most convenient method to calculate reaction processes, the close-coupling-state method automatically takes into account some of the long-range nonadiabatic effects and short-range correlations, although the extent is quite uncertain. It has been noted by Temkin[10] that this differential equation method (i.e., to expand the solution of an (N + 1) particle differential equation in terms of a complete set of known N-particle eigenfunctions, thus reducing the many-particle Schrödinger equation into a set of one-particle differential equations which then can be solved by numerical methods) seems to be the most natural way to include these nonadiabatic effects.

But the close-coupling-states method suffers on two points. First, it is difficult to assess the contribution of the atomic continuum states which must be omitted in the method. More serious is the method's inability to give correct long-range polarization potentials. As we mentioned before, a close-coupling between spherically symmetric states will give no polarization force at all. Even if we can close-couple <u>all</u> discrete states, the sizable contribution from the continuum state would still be missing, and we know from experience that a correct long-range potential is most important in any low-energy

atomic scattering.[10] In fact, the presence of the long-range polarization potential even completely changes the basic form of the effective-range formula for low-energy scatterings.[10A]

B. Optical-Potential Method

The so-called optical-potential method was first developed in nuclear scattering problems.[11] The basic idea is that we replace the complicated many-particle effect—which the incident particle experiences during the entire scattering process—by an equivalent single-body potential $\mathcal{V}$, the optical potential. The elastic scattering is then described by the simple one-particle Schrödinger equation

$$\left[E_0 - K - \mathcal{V}_-\right] \phi_0(x) = 0. \tag{2B-1}$$

In this approach all complicated many-body effects are absorbed in the optical potential $\mathcal{V}$, which is very hard to evaluate and is, in general, nonlocal. Moreover, the complicated optical potential can be determined completely only when the scattering problem itself is completely solved, a vicious circle sadly noted by Lippmann and Schey.[12]

A formal expression for the optical potential can be obtained readily and for atomic scattering it was first given by Mittleman and Watson.[13] However, the optical potential is not unique. Here we show one version of the potential that we shall derive in the next section. For scattering in the atomic channel Φ_0, we have

$$\mathcal{V}(x) = \left\langle 0 \middle| V + V \frac{(I - \pi_0)}{a^+} V + V \frac{(I - \pi_0)}{a^+} V \frac{(I - \pi_0)}{a^+} V + \cdots \middle| 0 \right\rangle , \tag{2B-2}$$

where

$$a^+ = (E - K - H_A + i\eta). \tag{2B-3}$$

The quantity η is a positive infinitesimal to insure an outgoing wave boundary condition. The identity operator is denoted by I and π_0 is the projection operator onto the initial atomic state Φ_0; i.e., $\pi_0 = |0\rangle\langle 0|$. The operator $(I - \pi_0)$ then forbids the atomic state Φ_0 to appear in any virtual intermediate states.

The optical-potential expression (2B-2), while exact in principle, is extremely difficult to evaluate. In practice we can only estimate the second-order term

$$\left\langle 0 \left| V \frac{(I - \pi_0)}{a^+} V \right| 0 \right\rangle$$

and neglect higher terms. In practice one also assumes that the scattered particle changes very little in energy in each virtual transition (i.e., $E_{p_0} - K \approx 0$ in a^+). Therefore we replace a^+ in the propagator by

$$d^+ = \epsilon_0 - H_A + i\eta \; ; \qquad (2B\text{-}4)$$

this is commonly called the adiabatic approximation.

When we make this adiabatic approximation, the second-order term of the optical potential is then exactly equal to the second-order energy-perturbation term when the atom is under the influence of a static point charge. If the scattered particle is far from the atom this term yields the familiar dipole polarization potential $[-(\alpha/2)/r^4]$. When the particle is near the atom even this adiabatically approximated term becomes hard to evaluate. One usually introduces some kind of cutoff parameter in the potential, such as the parameter d in the much-used Buckingham potential,[14]

$$\mathcal{V}^{(2)} = - \frac{\alpha/2}{(r^2 + d^2)^2} \; . \qquad (2B\text{-}5)$$

We note that, in the language of virtual transitions, the close-coupled-states method differs widely from the optical-potential method. The former method essentially assumes that only a few of the atomic states (the N states in the close-coupling scheme) are important, and that the effective potential allows virtual transitions to all orders only among these states while other atomic states do not contribute at all. The latter method, on the other hand, assumes that all atomic states are equally important and may be equally excited (virtually). The expression $\mathcal{V}$ in the optical equation is an iterative expansion in the

number of virtual transitions. For example, in the second-order term in $\mathcal{V}$, the atom is allowed to be excited (virtually) to any other atomic state once and only once (including the continuum) before being deexcited back to the ground state. In the adiabatic limit, however, this second-order term gives the correct long-range polarization potential, the so-called dispersion potential.

To recapitulate: we see in practice that the optical-potential method gives the correct polarization force at large distances but is completely incapable of accounting for nonadiabatic behavior or any short-range correlation effects. The close-coupled-states method, on the contrary, does partially allow for the short-range and non-adiabatic effects, but in general is unable to give the correct long-range polarization potential.

III. FORMAL DERIVATION OF THE GENERALIZED OPTICAL-POTENTIAL METHOD

In this section we shall formally derive the generalized optical-potential method, which—as we shall show—does contain the advantages of both methods described in the preceding section.

A. Derivation Without the Pauli Principle

The solution ψ of the atomic-scattering process is given, in the Lippmann-Schwinger formalism,[15] by the integral equation in operator form:

$$\psi = \chi + \frac{1}{a^{+}} V \psi, \tag{3A-1}$$

where χ is the initial wave function before interaction, $\chi = \Phi_0(z) \exp(i\underset{\sim}{p}_0 \cdot \underset{\sim}{x})$. The symbol a^{+} is from

$$a^{+} = E - H_A - K + i\eta, \tag{3A-2}$$

where symbols H_A, K, E are as defined in previous sections. The positive imaginary infinitesimal term $+i\eta$ is used simply to indicate that the "propagation" $1/a^{+}$ under an integral sign is equivalent to

$$\frac{\mathcal{P}}{E - H_A - K} - i\pi\delta(E - H_A - K),$$

where $\mathcal{P}$ means the Cauchy principal value. This formal device insures the correct boundary condition of the scattering problem—that there will be an outgoing spherical wave.

Next, we introduce a projection operator Π_N which is a sum of projection operators π_n onto the atomic state Φ_n:

$$\Pi_N = \sum_n^N \pi_n = \sum_n^N \left| n \right\rangle \left\langle n \right| . \tag{3A-3}$$

The choice of these N states depends on which N atomic states we wish to close-couple. Of course it must include the initial state Φ_0.

Let us define the generalized optical wave function

$$\psi_c = \Pi_N \psi . \tag{3A-4}$$

Clearly, within the N closely-coupled atomic channels, ψ_c describes the same scattering processes as ψ, but it contains no other channels as does ψ. Thus, if we are only interested in the reaction processes in the N channels, we may as well solve for ψ_c instead of ψ.

We now seek an integral expression for ψ_c:

$$\psi_c = \chi + \frac{1}{a^+} \mathcal{V} \psi_c , \tag{3A-5}$$

where $\mathcal{V}$ is the generalized optical potential in which we are interested.

Multipling Eq. (3A-1) by Π_N from the left, since a^+ and Π_N commute (Appendix A), we get

$$\psi_c = \chi + \frac{1}{a^+} \Pi_N \; V \psi . \tag{3A-6}$$

By combining Eqs. (3A-1) and (3A-6),

$$\psi = \psi_c + \frac{1}{a^+} (1 - \Pi_N) \; V \psi . \tag{3A-7}$$

Now, we define the operator F by

$$\psi = F \psi_c . \tag{3A-8}$$

Substituting Eq. (3A-8) into Eq. (3A-6) and comparing the resulting equation with (3A-5), we obtain the generalized optical potential

$$\mathcal{V} = \Pi_N V F . \tag{3A-9}$$

To derive the expression F, we simply substitute Eq. (3A-8) into Eq. (3A-7) and obtain

$$F = \Pi_N + \frac{1}{a^+} (I - \Pi_N) \; V F . \tag{3A-10}$$

Equations (3A-9) and (3A-10) completely determine the generalized optical potential $\mathcal{V}$. Expanding F, we have, more explicitly,

$$\mathcal{V} = \Pi_N \left[V + V \frac{(I - \Pi_N)}{a^+} V + V \frac{(I - \Pi_N)}{a^+} V \frac{(I - \Pi_N)}{a^+} V + \cdots \right] \Pi_N . \tag{3A-11}$$

Now, ψ_c satisfies [from Eq. (3A-5)] the Schrödinger equation

$$(a^+ - \mathcal{V})\psi_c = [E - H_A - K - \mathcal{V}]\psi_c = 0. \tag{3A-12}$$

Since $\mathcal{V}$ has the projection operator Π_N on both sides (i.e., it has nonvanishing matrix elements among the N atomic states only), the wave function ψ_c, correspondingly, is then a column matrix with nonzero elements for those N states. Thus, without losing generality, we may write ψ_c as

$$\psi_c = \sum_n^N \phi_n(x) \; \Phi_n(z) . \tag{3A-13}$$

Substituting this into Eq. (3A-12) and integrating over the atomic wave functions Φ_n, we obtain the set of N coupled equations.

$$(E_n - K)\, \phi_n(x) = \sum_m^N \mathcal{V}_{nm}(x)\, \phi_m(x) \tag{3A-14}$$

for $n = 0, \cdots, N$.

Where the matrix element $\mathcal{V}_{nm}$ is, more explicitly,

$$\mathcal{V}_{nm} = V_{nm} + \sum_{j \neq N} V_{nj} (E - \epsilon_j - K + i\eta)^{-1} V_{jm} + \cdots \tag{3A-15}$$

for n, m in N.

Equation (3A-14) represents the fundamental result of this generalized optical-potential method. Within those N channels, it is a formally correct and exact solution to the actual scattering problem.

We will now dwell on this for a while and make several comments on this method. First we would like to show here the connection of this method with the two conventional approaches mentioned in Sec. II.

The choice of the N states to be close-coupled is arbitrary. If we let N become larger, in the limit N includes the complete set of atomic states Φ_n. Then Π_N approaches the identity operator and $\mathcal{V}_{nm}$ becomes simply V_{nm}, the first term in Eq. (3A-15). Equation (3A-14) becomes an infinite set of coupled equations, which is identical to the eigenfunction expansion result. On the other hand if we were to let N contain only one atomic state Φ_0, Eq. (3A-14) becomes a single, uncoupled, one-particle Schrödinger equation, which is just the ordinary optical-potential equation for elastic scattering. Thus we see that ours is a more refined scheme, or a hybrid type, which contains the two methods in the above-mentioned extreme limits.

Next, we turn to the necessary approximations on optical potentials $\mathcal{V}_{nm}$ in solving Eq. (3A-14). If we retain only the first term on the right-hand side of (3A-15), i.e., $\mathcal{V}_{nm} = V_{nm}$, we find that our method yields, in this lowest approximation, the usual method of close-coupled-states approximation [Eq. (2A-9)].

However, we shall be able to include the adiabatically approximated second term in (3A-15), which may actually dominate the first term in some regions:

$$\mathcal{V}_{nm} \approx V_{nm} + \sum_{j \neq N} V_{nj} \frac{1}{\epsilon_0 - \epsilon_j} V_{jm} . \tag{3A-16}$$

For example, if Φ_n and Φ_m are both bound and spherically symmetric, V_{nm} will be exponentially decreasing at large distances while the second term will yield the long-range $1/r^4$ polarization tail.

In analogy to the distorted-wave approximation, Eq. (2A-13), we shall have the optically-distorted wave approximation:

$$\left.\begin{aligned} \left[E_0 - K - \mathcal{V}_{00}\right] \phi_0 &= 0 \\ \left[E_n - K - \mathcal{V}_{nn}\right] \phi_n &= \mathcal{V}_{n0} \phi_0 \end{aligned}\right\} . \tag{3A-17}$$

Here the incoming particle comes in a polarized atomic field, makes one "optical" transition, and leaves in the distorted field of the excited

atom in the nth state—this is much more realistic than the corresponding Eq. (2A-13).

In practical calculations, our philosophy of approach is as follows. We shall include as many atomic states in N as the situation demands, and as the capacity of the electronic computer allows. They may include the initial and the final states of a particular reaction process in which we are interested, as well as their degenerate states, if any. The contribution of the other atomic states (including the continuum) enters adiabatically through the generalized optical potentials. Since we shall always have the correct adiabatic long-range polarization potential through the $\mathcal{V}$'s, the choice of the optically close-coupled states should be such that the nonadiabatic and short-range correlation effects be best taken into account by them.

Thus we see the generalized optical-potential method combines the practical advantages of both the usual optical-model-potential method and the close-coupled eigenfunctions approach. It also justifies theoretically the ad hoc potential terms used by many authors.[6, 16] We also point out here that the ensuing equations are similar to the usual close-coupling-approximation equations and are no more difficult to solve.

B. Modification for Electron–Hydrogen-Atom Scattering

We now apply the generalized optical-potential method to low-energy electron–hydrogen-atom scattering. The choice is made for the following reasons. First of all it is the simplest atomic-scattering problem of real physical interest. The complete atomic-hydrogen wave functions are known, so that all approximations must come only from the generalized optical potentials. More important, there exist rather thorough theoretical investigations in the literature for this particular case. With more refined experimental results soon available, we will be able to compare and to assess the merits of various theoretical approximations. In turn, we will use them with greater confidence in other more complicated problems.

However, the incoming particle in this case is an electron and the Pauli principle demands explicit antisymmetrization in the trial wave functions. This requires certain formal modifications in the derivation of the generalized optical-potential method. For our electron-hydrogen case, it is particularly simple and we shall include the Pauli principle in the rest of this section.

It is well known that when the spin-dependent force is neglected, the effect of the spin is only a kinematic one. In our two-electron case, it simply breaks the problem into two separate cases in the coordinate space: the singlet (total spin zero) and the triplet (total spin one) scattering. The singlet spatial wave function $\psi^{+}(1, 2)$ is symmetric under the exchange of the spatial coordinates of the two electrons 1 and 2, while the triplet wave function $\psi^{-}(1, 2)$ is antisymmetric:

$$\psi^{\pm}(1, 2) = \pm\, \psi^{\pm}(2, 1). \tag{3B-1}$$

When the incoming electron beam is unpolarized the total cross section is given as

$$\sigma = \frac{1}{4}\,(\sigma^{+} + 3\sigma^{-}). \tag{3B-2}$$

We use an explicit symmetric or antisymmetric two-particle othonormal basis constructed from the complete set of the single-particle orthonormal hydrogen wave functions Φ_n. We define

$$\left| m,\ n\pm \right\rangle = \frac{1}{\sqrt{2}}\ \theta(m - n)\left[\Phi_m(1)\ \Phi_n(2) \pm \Phi_m(2)\ \Phi_n(1)\right], \tag{3B-3}$$

where

$$\theta(m - n) = \begin{cases} 1 & m > n \\ 1/\sqrt{2} & m = n \\ 0 & m < n\,. \end{cases}$$

The $\left|m, n\pm\right\rangle$'s form a complete orthonormal basis in their respective symmetrized or antisymmetrized subspace:

$$\left\langle p,\ q\pm \middle|\ m, n\pm\right\rangle = \delta_{pm}\ \delta_{qn}, \tag{3B-4}$$

and the identity operator is $I = I^{+} + I^{-}$, where

$$I^{\pm} = \sum_{n,} \sum_{m \geqslant n} \left| m, n\pm \right\rangle \left\langle m, n\pm \right| . \qquad (3B\text{-}5)$$

The total wave function $\psi^{\pm}(1, 2)$ can of course be expanded on this basis:

$$\psi^{\pm}(1, 2) = \sum_{n, m \geqslant n} \left| m, n\pm \right\rangle \left\langle m, n\pm \middle| \psi^{\pm} \right\rangle . \qquad (3B\text{-}6)$$

By definition m is always larger than or equal to n in $\left| m, n\pm \right\rangle$. We can then, without ambiguity, define state $\left| m, n\pm \right\rangle$ as being one in which the atomic electron is in the state n while the scattered electron is in state m. The definition of $\theta(m - n)$ also implies a definite ordering scheme in designating the complete set of hydrogenic states Φ_m. One readily sees that the ordering within the N atomic states to be close-coupled does not matter since they enter into the resulting close-coupled equations equally. Neither does the ordering among other atomic states have any effect, since the other states enter into the resulting equation via the generalized optical potentials only, and they also enter equally.

Now, the relative position between the N atomic states and the rest states in this ordering scheme is dictated by our wish that the real asymptotic wave of the outgoing scattered particle in each atomic channel n of N be correctly and completely projected out by the projection operator

$$\pi_n = \sum_{m \geqslant n} \left| m, n\pm \right\rangle \left\langle m, n\pm \right| \qquad (3B\text{-}7)$$

when operating on the complete wave function $\psi^{\pm}(1, 2)$. This requirement will be met as long as all continuum states are larger than the N states in the ordering. However, the most convenient choice (the one we shall make) is to put the N atomic states to be close-coupled as the lowest N states in the ordering scheme. We call the operator π_n defined in Eq. (3B-7) the projection operator onto the "atomic state" n.

Finally, one may also wonder whether the ordering within the N atomic states would have effect on the "scattered-particle state." As will be shown later, there will be no restrictions on the scattered particle because of the ordering.

We now turn to electron-hydrogen scattering. Let the atom be in ground-state zero and the incoming electron with initial momentum p_0. The correct integral equation for the total wave function is[13A]

$$\psi^{\pm}(1, 2) = \left| p_0, 0\pm \right\rangle + \frac{1}{a^{+}} V_{12} \psi^{\pm}(1, 2), \tag{3B-8}$$

where V_{12} is the interelectron interaction e^2/r_{12} and

$$\begin{aligned} a^{+} &= E - \left[K_1 + V_N(1) + K_2 + V_N(2)\right] + i\eta , \\ E &= \frac{p_0^{\,2}}{2m} + \epsilon_0 . \end{aligned} \tag{3B-9}$$

Note that the definition of a^{+} here is different from that in Subsec. III-A and is symmetric with respect to electrons 1 and 2. The propagator $1/a^{+}$ is then diagonal on the basis we have just defined. However, the scattered particle's initial state is a Coulomb wave function and thus contains the associated logarithmic phase shift. We can get around this trouble by considering it as a screened Coulomb wave function with a limit of zero screening. In any case, these functions are used to obtain the expressions for the generalized optical potentials, and no actual difficulty (because of the long-range nature of the Coulomb potentials) shall arise in the final resulting equations. We would also like to point out that this method works only for the electron-hydrogen scattering case because of its particular simplicity.

Let Π_N be a projection operator onto the subspace where the "atomic state" is in any of the N states in the close-coupling scheme:

$$\Pi_N = \sum_{n}^{N} \pi_n = \sum_{n}^{N} \sum_{m \geq n} \left| m, n\pm \right\rangle \left\langle m, n\pm \right| . \tag{3B-10}$$

Following the general development of Subsec. III-A, we define the generalized optical wave function

$$\psi_c^{\pm} = \Pi_N^{\pm} \psi^{\pm} \tag{3B-11}$$

and seek an integral equation for $\psi_c^{\pm}$:

$$\psi_c^{\pm} = \left| p_0, 0\pm \right\rangle + \frac{1}{a^{\mp}} \mathcal{V}^{\pm} \psi_c^{\pm} . \tag{3B-12}$$

If we let $\psi^{\pm} = F^{\pm} \psi_c^{\pm}$, Eq. (3B-8) and Eq. (3B-11) yields

$$\psi_c^{\pm} = \left| p_0, 0\pm \right\rangle + \frac{1}{a^{\mp}} \Pi_N^{\pm} V_{12} F^{\pm} \psi_c^{\pm} . \tag{3B-13}$$

As before, comparing Eq. (3B-12) and Eq. (3B-13) and demanding consistency, we obtain

$$\left.\begin{aligned} \mathcal{V}^{\pm} &= \Pi_N^{\pm} V_{12} F^{\pm} \\ F^{\pm} &= \Pi_N^{\pm} + \frac{(1^{\pm} - \Pi_N^{\pm})}{a^{\mp}} V_{12} F^{\pm} \end{aligned}\right\} . \tag{3B-14}$$

Equations (3B-14) give the explicit expression of the generalized optical potential we desire. Since the atomic states N are bound and are the lowest in the ordering scheme, $\psi_c^{\pm}$ contains the same asymptotic expressions in those N atomic channels as $\psi^{\pm}$; and from Eq. (3B-11) we see $\psi_c^{\pm}$ satisfies the Schrödinger equation

$$\left\{ E - \left[K_1 + V_N(1) + K_2 + V_N(2) + \mathcal{V}^{\pm} \right] \right\} \psi_c^{\pm} = 0. \tag{3B-15}$$

The state $\psi_c^{\pm}$ is explicitly symmetric or antisymmetric so we can write

$$\psi_c^{\pm}(1, 2) = \sum_n^N (1 + P_{12}) \phi_n(1) \Phi_n(2), \tag{3B-16}$$

P_{12} being an operator interchanging the coordinates of electrons 1 and 2. Equation (3B-16) has the same form as the trial wave function in the usual close-coupling approximation with exchange, but they differ in one respect: There are no restrictions on the scattered particle

wave function in the usual close-coupling approximation with exchange. But, because of the projection operators π_n that are used to define the generalized optical wave function ψ_c^+, the scattered-particle wave function ϕ_n in Eq. (3B-16) seems to have an additional restriction in that it will contain no components of the atomic wave functions Φ_m for all m lower than n in the ordering scheme [i.e., $\langle \phi_n(r) | \Phi_m(r) \rangle = 0$ for $m < n$]. By setting the N states as the lowest in the ordering scheme, all other states will be higher than the N states and so may be contained in ϕ_n's. Even so, the ϕ_n's still seem to have the restriction that $\langle \phi_n | \Phi_m \rangle = 0$ for $n > m$ for m, n both in N. This would still be very cumbersome if one is to solve the ϕ_n's numerically. However, the fact that we are summing all N atomic states in Eq. (3B-16) makes it possible to relax even this last restriction (see Appendix D).

The dimensionless units used throughout this work are the atomic units. That is:

$\hbar = 1$, $c = 137$,

Mass unit = electron mass, or $m_e = 1$,

Charge unit = electron charge, or $e = 1$,

Length unit = Bohr radius (0.53×10^{-8} cm),

Energy unit = 27.2 eV = $2|\epsilon_0|$,

$E = 13.6k^2$ eV.

We now turn to the generalized optical potentials in Eq. (3B-15). The atomic states we choose to be close-coupled are 1s, 2s, and 2p states. Inasmuch as the generalized optical potentials are used to give the correct long-range polarization potential, they will be evaluated to second order only for those matrix elements whose second-order direct term dominates the first-order term $\langle n | V_{12} | m \rangle$ at large distance. This includes the matrix elements $\mathcal{V}^{(2)}_{1s,1s}$, $\mathcal{V}^{(2)}_{1s,2s}$, ($\mathcal{V}^{(2)}_{2s,1s}$), and $\mathcal{V}^{(2)}_{2s,2s}$. Here again we resort to the adiabatic approximation by replacing a^+ by $d^+ = \epsilon_0 - K_2 + V_N(2) + i\eta$.

Now a mathematically equivalent statement for this adiabatic approximation assumption is that in virtual transitions the matrix elements $\langle q, n | V | p_0, 0 \rangle$ contribute mainly from those $|q, n\rangle$ states for which $E_{p_0} - E_q \approx 0$, so that we may omit the

$[E_{p_0} - (K_1 + V_1)]$ term in $a^{\dagger}$. This means that the contributing states $\Phi_q(1)$ of the scattered particle are continuum states because the initial state $\Phi_{p_0}(1)$ is a continuum. Since the atomic states $\Phi_0(2)$ and $\Phi_n(2)$ are mostly bound and since they are quite different from the contributing Φ_{p_0} and Φ_q's, the adiabatic approximation actually implies that the exchange term $\langle n, q | V | p_0, 0 \rangle$ will be very small. Thus, when the adiabatic approximation is valid, we may neglect the exchange terms in the virtual states and replace $(I - \Pi_N)$ in $\mathcal{V}^{(2)}_{n,m}$ by

$$\left[I - \sum_{n}^{N} \Phi_n(2)\, \Phi_n^{*}(2) \right] .$$

With these approximations, we proceed to evaluate the second-order potential terms $\mathcal{V}^{(2)}_{1s,1s}$, $\mathcal{V}^{(2)}_{1s,2s}$, and $\mathcal{V}^{(2)}_{2s,2s}$. The $\mathcal{V}^{(2)}_{1s,1s}$ term is the most important since it enters directly into the potential for our elastic scattering while the other two have second-order effect only. The work of Delgarno and Lynn[33] enables us to evaluate this adiabatically approximated $\mathcal{V}^{(2)}_{1s,1s}$ exactly if we want to. However, there is no point in doing so since the adiabatic condition itself will not hold when the particle gets very near the atom. Thus we shall only use the leading $1/r^4$ term for the long-distance behavior, both for $\mathcal{V}^{(2)}_{1s,1s}$ and for $\mathcal{V}^{(2)}_{2s,2s}$. In $\mathcal{V}^{(2)}_{1s,2s}$ we use the Buckingham-type potential with the parameter d such that when it is expanded the coefficients of the $1/r^4$ and $1/r^6$ terms will agree with those obtained by the multipole expansion method. At small r—where the adiabatic condition is to be abandoned—we introduce a cutoff factor $(1 - e^{-ar})^5$, $a = 0.5$, in the manner of Allison et al.[17] This factor will insure that the $\mathcal{V}$'s vanish at $r = 0$. It was found that the results are not very sensitive to the small variation of the parameter "a" (Table I). The second-order optical potentials used in our calculations are

$$\mathcal{V}^{\pm(2)}_{1s,1s} = (1 - e^{-r/2})^5 \left(- \frac{0.77}{r^4} \right),$$

$$\mathcal{V}^{\pm(2)}_{2s,1s} = \mathcal{V}^{\pm(2)}_{1s,2s} = (1 - e^{-r/2})^5 \left[- \frac{2.47}{(r^2 + 0.935)^2} \right],$$

$$\mathcal{V}^{\pm(2)}_{2s,2s} = (1 - e^{-r/2})^5 \left(- \frac{10.52}{r^4} \right) .$$

Table I. Phase shifts with various values of parameter a.[a]

	k^2	a = 0.4	a = 0.5	a = 0.6
δ^{0+}	0.05	1.8970	1.8974	1.8976
	0.30	1.0255	1.0262	1.0269
	0.60	0.7926	0.7943	0.7955
δ^{1-}	0.10	0.1163	0.1165	0.1166
	0.30	0.2865	0.288	0.289
	0.60	0.3988	0.3995	0.4001
δ^{2+}	0.10	0.063	0.063	0.063
	0.30	0.0327	0.0328	0.0328
	0.60	0.0631	0.0633	0.0634

[a]Values of δ are in radians.

The close-coupled integro-differential equations from substitution of Eq. (3B-16) into Eq. (3B-15) can be further reduced to close-coupled radial equations only by partial-wave theory, as was first done by Percival and Seaton.[18] In Appendix B we give the resulting radial equations and other pertinent quantities of this partial-wave reduction. The radial equations thus obtained are subsequently numerically integrated on an IBM 7090 computer, yielding partial-wave phase shifts directly. In Appendix C we give a brief description of the numerical techniques used. Aside from minor modifications, the code we used was that of Burke and Schey.[21]

IV. NUMERICAL RESULTS AND DISCUSSION

By using the generalized optical-potential method, the close-coupling scheme, and the generalized optical potentials described in Subsec. III-B, the phase shifts for the total angular momentum states $L = 0, 1, 2, 3$ have been evaluated for both spin states in the energy range below the threshold for excitation of the second target quantum level ($k^2 = 0.75$, or 10.2 eV). Results of these phase shifts (in radians) are presented in Table II. We encountered convergence difficulties near zero energy, and also for energies near the second quantum-level threshold, where resonance-type effects seem to exist in many spin and angular-momentum states.

We shall analyze and discuss the results in each angular-momentum and spin state separately. As has been emphasized, our aim is to gain a better understanding of the mechanisms involved in the low-energy atomic-scattering process, their relative importance, and their range of validity.

A. S-Wave (L = 0) Phase Shift

With each particular angular momentum L is associated a centrifugal barrier $L(L + 1)/r^2$ in the radial equation. This centrifugal barrier will keep the incoming particle farther away from the atom as L increases. We thus expect the short-range correlation effect due to the interelectron interaction e^2/r_{12} to play its largest role in this singlet S-wave case. In Fig. 1 we present our results as well as the variational calculations of Schwartz,[9] the static approximation with exchange of John[19] (1s), the (1s-2s) exchange approximation results of Smith et al.,[20] the (1s-2s-2p) close-coupling approximation with exchange by Burke and Schey,[21] and the results of Temkin's[10] nonadiabatic theory. We also include the curve δ_0, the zeroth-order phase shift from Temkin's calculation.

The result of Schwartz[9] should be rather accurate since it is obtained by a variational treatment where the trial wave function has been adequately represented (up to 50 terms) to take into account the short-range correlations. That his result is trustworthy is further

Table II. Phase shifts, in radians, for singlet (δ^{L+}) and triplet (δ^{L-}) L = 0, 1, 2, 3 states.

k^2	δ^{0+}	δ^{0-}	δ^{1+}	δ^{1-}	δ^{2+}	δ^{2-}	δ^{3+}	δ^{3-}
0.01	-0.6363							
0.02	2.2799							
0.03	2.1166				0.003985			
0.04	1.9930							
0.05	1.8974		0.016	0.0586	0.006347	0.006723		
0.10	1.562	2.485		0.1165	0.01227	0.01348	0.004270	0.004274
0.20	1.215	2.2066	-0.0201	0.206	0.0230	0.02555		
0.30	1.0262	1.9616	-0.027	0.288	0.0328	0.03586		
0.40	0.9059	1.8846	-0.035	0.3455	0.0419	0.04497	0.01511	0.01484
0.50	0.8363	1.7766	-0.0456	0.3761	0.0515	0.05324		
0.60	0.7943	1.6915	-0.0480	0.3995	0.0633	0.0610		
0.65	0.8020		-0.0436	0.4123	0.0716			
0.66	0.8108							
0.67	0.8285							
0.68	0.8648							
0.69	0.9754							
0.70	≈2.3			0.4495	0.08497	0.06826	0.02513	0.02559
0.71	0.5440							
0.72	0.6554							
0.73	0.7009							
0.74	0.7363				0.1442	0.07118		
0.0	A = 6.52172							

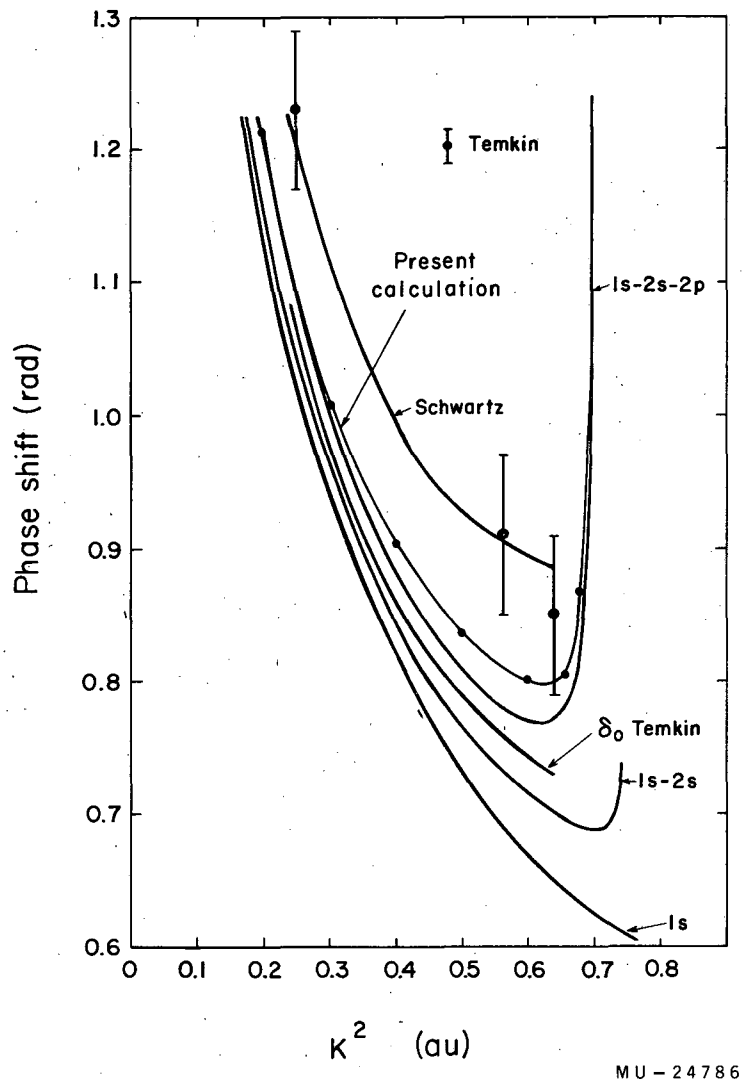


Fig. 1. The singlet S phase shift as a function of k^2, as given by various calculations.

augmented by its close agreement with the result of Temkin,[10] who used a novel and entirely different approach of nonadiabatic expansion. We then see that our result makes only about half of the correction from the (1s) static result toward the "correct" result of Schwartz.

The difference between (1s) and (1s-2s) curves is due entirely to the better case of the short-range effect by the inclusion of the 2s state, while the difference between the (1s-2s) curve and the (1s-2s-sp) curve is due to the contribution of the 2p coupling to the short-range effect and also to the inclusion of 66% of the long-range polarization force by the 2p states.[22] That those two differences are almost equal suggests that the corrections are more due to the short-range effect than the long-range force. This is also manifested in the small improvement of our result over the (1s-2s-2p) result, which is mainly due to the addition of the 34% of the correct long-range force in our calculation.

It was observed by Burke and Schey[21] by direct calculations that the addition of more bound atomic states in the usual close-coupling scheme improve results only slowly. This can also be seen by the small difference between the (1s-2s) curve and Temkin's δ_0 curve. The δ_0 result is effectively a close-coupling approximation of all s states, so the small difference represents the contributions from 3s, 4s, $\cdots$, and all the continuum s states. Since our calculation has included the correct long-range force, the large difference between our result and Schwartz's correct result is entirely due to the short-range effect, and the major part of it must come—from the above argument—from the contribution of the atomic continuum states.

If we take the difference between our result and the (1s-2s-2p) close-coupling result as <u>entirely</u> due to the effect of 34% of the long-range polarization potential, we can make the following estimates: In the general energy range we are now dealing with, the long-range force gives about 30% of the correction from the (1s) result to the correct (Schwartz's) result. The remaining 70% comes from the short-range effect, the bound states contributing about 35% and the continuum states contributing about 35%.

Above $k^2 = 0.65$ the phase shifts increase sharply, exhibiting a resonance effect similar to the results of Burke and Schey.[21] Following their work, we analyze this resonance phenomenon by decomposing the phase shift into two parts: the slow-varying nonresonant potential part δ_{pot} and the resonant part δ_{res}, $\delta_{tot} = \delta_{res} + \delta_{pot}$. Then the total cross section is given by

$$\sigma_{tot} = (\pi/k^2) \left| A_{res} + A_{pot} \right|^2 , \tag{4-1}$$

where

$$A_{res} = \exp(2i\ \delta_{pot}) \left[\exp(2i\ \delta_{res}) - 1 \right] ,$$

$$A_{pot} = \exp(2i\ \delta_{pot}) - 1 .$$

Next, we define the resonant part of the singlet S-wave cross section by

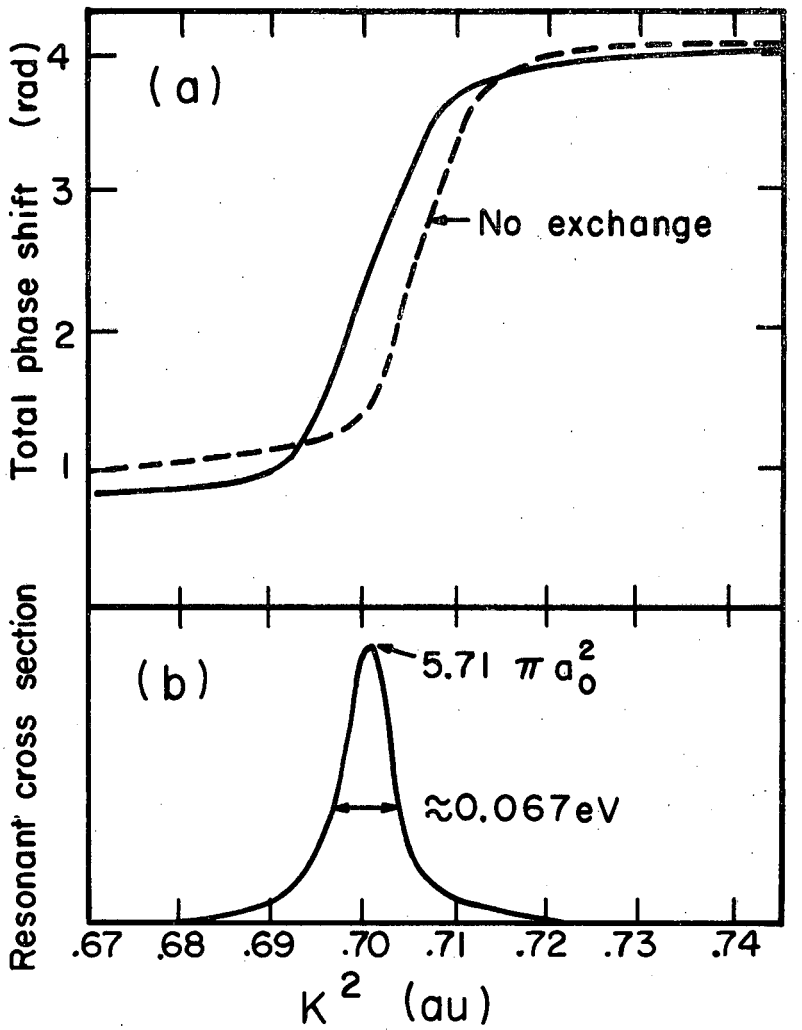
$$\delta_{res} = \left(\frac{\pi}{k^2} \right) \left| A_{res} \right|^2 = (4\pi/k^2) \sin^2 \delta_{res} . \tag{4-2}$$

If we give this cross section a standard Breit-Wigner type fit,

$$\delta_{res} = \frac{4\pi}{k^2} \frac{\frac{1}{4} \Gamma^2}{(E - E_{res})^2 + \frac{1}{4} \Gamma^2} , \tag{4-3}$$

we find the resonance energy $E_{res} = 9.51$ eV ($k^2 = 0.70$) and the full width $\Gamma = 0.067$ eV. This is to be compared with the results obtained by Burke and Schey[21] for the similar phenomenon in their (1s-2s-sp) close-coupling approximation calculation, which gives $E_{res} = 9.61$ eV ($k^2 = 0.707$) and $\Gamma = 0.109$ eV. Our resonance energy lies slightly lower and the resonance width is narrower. Thus, if this resonance effect is real, it would be even harder to observe. The resonance peak in the total cross section occurs, of course, at $\delta_{tot} = \pi/2$, or at $k^2 = 0.696$ ($E_{res} = 9.45$ eV). Figure 2(a) shows the singlet S-wave phase-shift curve in this energy range, and Fig. 2(b) gives the corresponding resonant part of the cross section, σ_{res}.

This resonant behavior in the phase shift is not limited to the singlet S-wave case alone but seems to exist for many spin and angular



MU-31175

Fig. 2(a). The singlet S phase shift as a function of k^2.
(b). The corresponding resonant cross section.

momentum states. Similar behavior was also found in Burke and Schey's result, as well as in other calculations based on the eigenfunction expansion approach. We leave this subject for the time being but will comment and speculate on the origin of this phenomenon further, in the final section.

Next, we go on to the zero-energy case. We obtained for the singlet S-wave a scattering length of 6.520. This is to be compared with the value of 6.742 obtained by Burke and Schey,[21] whose method of (1s-2s-2p) close-coupling with exchange approximation is very close to ours except for the long-range force, as mentioned before. The best value of this scattering length is an upper bound of 5.965 ± 0.003, obtained by Schwartz[9] by variational approach with up to 60 parameters in the trial wave function. Since our method does include the correct adiabatic long-range potential, the still-quite-appreciable difference between our result and that of Schwartz seems to come from the breakdown of adiabatic condition at midranges and, probably more important, from correlation effects at short ranges.

In the analysis of low-energy nucleon-nucleon scattering data, the so-called effective-range theory has been proven to be very useful. According to this theory, the low-energy behavior of the S-wave scattering can be described by the effective-range approximation formula:

$$k \cot \delta_0 = -\frac{1}{A} + k^2 \frac{r_0}{2} + \mathcal{O}(r^4) \qquad (4\text{-}4)$$

where A is the scattering length, δ_0 is the S-wave phase shift for incoming-particle momentum k, and the constant r_0 is the so-called effective range.

O'Malley et al.[23] have reexamined the effective-range theory in detail and found that the usual simple formula as shown above is actually not valid for scattering containing long-range potentials such as in our case. Instead, for a long-range polarization potential $(-\beta^2/2r^4)$, the modified effective formula is given as[23]

$$k \cot \delta_0 = -\frac{1}{A} + \frac{\pi\beta^2}{3A^2} k + \frac{4\beta^2}{3A} k^2 \ln\left(\frac{\beta k}{4}\right)$$

$$+ \left[\frac{1}{2} r_0 + \frac{\pi\beta}{3} + \frac{20\beta^2}{9A} - \frac{8\beta^2}{3A} \psi\left(\frac{3}{2}\right) - \frac{\pi\beta^3}{3A^2} - \frac{\pi^2\beta^4}{9A^3}\right] k^2$$

$$+ \mathcal{O}(k^4), \qquad (4\text{-}5)$$

where $\beta^2 = 4.5$ in our case and $\psi(3/2) = \Gamma'(3/2)/\Gamma(3/2) = 0.0365$.

The above modified effective-range formula is rather complicated, and it differs from the ordinary one mainly by the presence of the k term and the $(k^2 \ln k)$ term. One may obtain the scattering length A from Eq. (4-5) by any two sets of low-energy data. Also a comparison between the values of A thus obtained with the result of 6.520 from direct numerical calculation enables one to estimate the energy region where this effective-range formula is useful. In Table III we give such a comparison and from that we conclude that the effective-range expansion in atomic scattering, due to the long-range nature of the potential involved, is rather "ineffective" and its range of usefulness is rather limited for $k^2 < 0.04$ (0.6 eV).

Table III. Comparison of extrapolated scattering length.[a]

Sets of k^2 values used	Extrapolated scattering length A
$k^2 = 0.2,\ 0.1$	8.101
$k^2 = 0.1,\ 0.05$	7.353
$k^2 = 0.05,\ 0.04$	7.296
$k^2 = 0.04,\ 0.03$	6.873
$k^2 = 0.03,\ 0.02$	6.767
$k^2 = 0.02,\ 0.01$	6.650

[a]Numerically integrated at $k = 0$, $A = 6.520$.

For the same angular-momentum wave, the triplet equations differ from the singlet equations only in the sign of the exchange potential. The magnitude of this exchange integral is an effective measure of the overlapping between the two electron wave functions. When the overlapping (i.e., the exchange-potential part) is small, the short-range correlation will be small, and the singlet and triplet phase shifts will tend toward each other.

In Fig. 3, our triplet S-wave phase shifts are plotted along with those of Schwartz,[9] the (1s) static result,[19] the (1s-2s) result,[20] as well as the (1s-2s-2p) result of Burke and Schey.[21] We first note that the triplet result is grossly different from the corresponding singlet result; this indicates the large contribution from the exchange integral (i.e., short-range correlation). We next note the surprisingly close agreement among all theoretical calculations in this case. This indicates that the effect of the polarization potential is negligible away from threshold and, more important, that the short-range correlation effect has been so well taken care of by the explicit spatial antisymmetry in the triplet wave functions as demanded by the Pauli principle that even the static (1s) approximation[19] gives remarkably good results. We mention here that the calculation on higher partial waves also shows that even the crudest approximations in the triplet case will take generally satisfactory account of the short-range correlations. The success of these triplet calculations led us in the final section to propose an alternative expansion form for the singlet trial wave functions.

Unfortunately for this triplet case—both in the zero-energy region and near the second quantum level—no convergent results could be obtained.

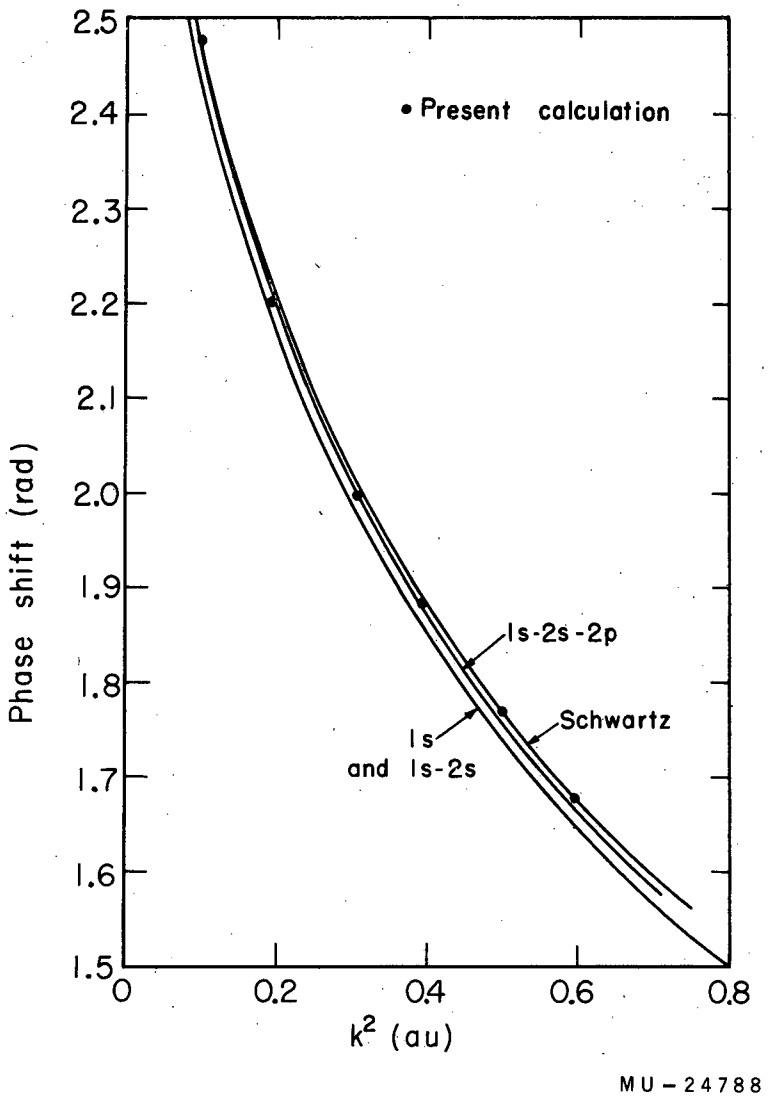


Fig. 3. The triplet S phase shift as a function of k^2, as given by various calculations.

B. P-Wave (L = 1) Phase Shifts

We present our singlet and triplet P-wave phase shifts in Figs. 4(a) and 4(b), respectively. They are also compared with—in addition to the (1s) and the (1s-2s) results[19,20]—the result of Bransden et al.,[6] with an adiabatic variational polarization potential; the result of Temkin and Lamkin's[24] polarized-orbit method; and that of Malik and Trefftz,[25] who used the one-body exchange equation with an ad hoc polarization potential.

Again, different calculation in the triplet case are more consistent than those in the singlet case. Again we have the contrasting behavior between the singlet phase-shift curve and the triplet curve, which indicates that the effects from short range are still substantial. In the triplet curve, the "improvement" of the (1s-2s) result[20] over the (1s) result[19] is rather large, while the addition of 2p states (hence 66% of total long-range polarization potential) in Burke and Schey's[21] calculation changes the phase shifts by a lesser amount. This supports our view that the short-range correlation effect still exerts a major influence over the whole energy range. Our result agrees well with that of Temkin and Lamkin's[24] polarized orbital method until we near the second quantum level, where a sharp increase of the phase shift again takes place, indicating a resonance effect similar to that in the singlet S-wave case.

The results of the singlet P-wave phase shifts are harder to analyze. The results of the (1s), (1s-2s), and (1s-2s-2p) calculations,[19,20,21] as well as ours, generally give negative phase shifts in this energy region while other calculations yield positive phase shifts. This seems to indicate that we are in a region where the influences of the short-range correlation and the long-range polarization become comparable. It is difficult to see whether the correct phase shifts should be positive or negative. However, in view of the small magnitudes of these phase shifts, it should cause little difference in the value of the total cross section.

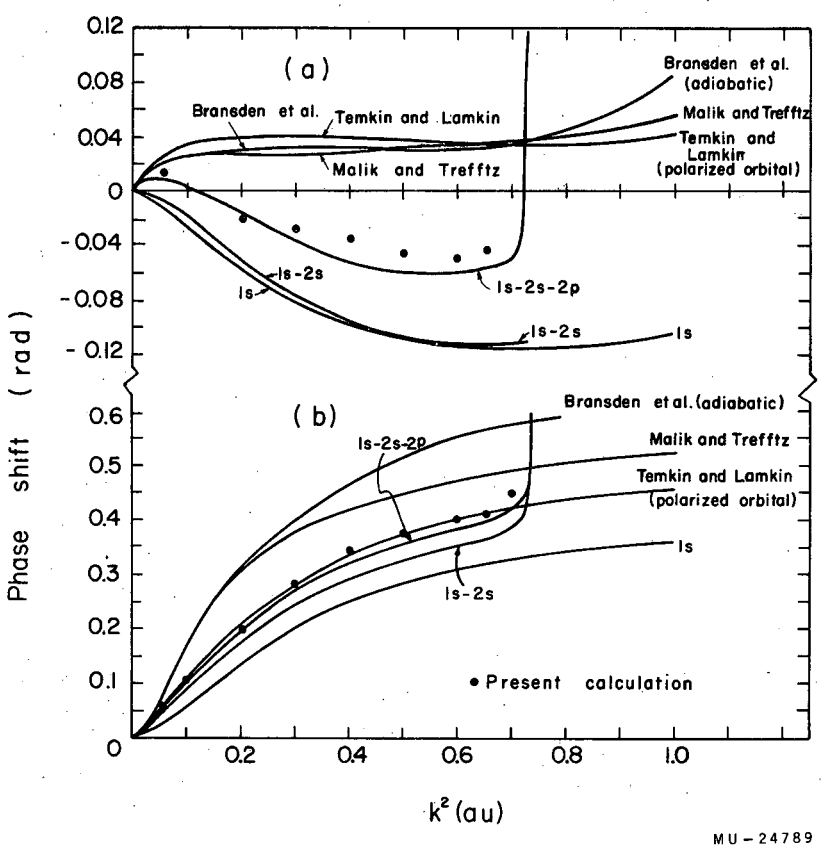


Fig. 4(a). Singlet P phase shift.
(b). Triplet P phase shift.

C. D-Wave (L = 2) Phase Shifts

Our results for the singlet and the triplet D-wave phase shifts are plotted in Figs. 5(a) and 5(b). We also show the results of John[19] (1s), of Smith et al.[20] (1s-2s), of Burke and Schey[21] (1s-2s-2p), as well as the results of Temkin and Lamkin's polarized-orbital-method[24] calculations. It has been shown[6, 23] that if a long-range $1/r^4$ potential is dominant, the phase shifts at low energies should vary linearly with the energy. It becomes immediately apparent, both from the similarity of our singlet result and the triplet result, and from the near-linear behavior of the phase-shift curve as a function of the k^2 value, that the centrifugal barrier has pushed the incoming-particle wave function sufficiently out so that the exchange potential becomes very small and the long-range polarization potential becomes dominant.

Calculations with no provisions to include the long-range potential such as the (1s) and the (1s-2s) results[19, 20] give phase shifts grossly different from other approximations with polarization included. Another indication of the dominance of the long-range force comes from the triplet case, where the ratio of the correction of the (1s-2s-2p) result[21] over the (1s-2s) result[20] to the correction of our result over the (1s-2s) result[20] is roughly equal to the ratio of the amount of the long-range polarization force included in the (1s-2s-2p) calculation to that in our calculation; i.e., 0.66/1. The singlet D-wave phase-shift curve begins to deviate from linearity above $k^2 = 0.6$ and rises sharply as it nears the second quantum level threshold—another resonance effect similar to those found in Burke and Schey's calculation.[21]

D. F-Wave (L = 3) and Higher-Order Phase Shifts

The analysis in D-wave phase shifts shows that the long-range polarization potential becomes the predomiant factor in the scattering process for the L = 2 waves. We then expect it would be even more so for higher-order partial waves. The results of our calculation on the F-wave phase shifts readily confirm this. Throughout our entire energy range the corresponding singlet and triplet phase shifts differ by less than 2% (see Table I), which shows that the exchange potential is negligibly small.

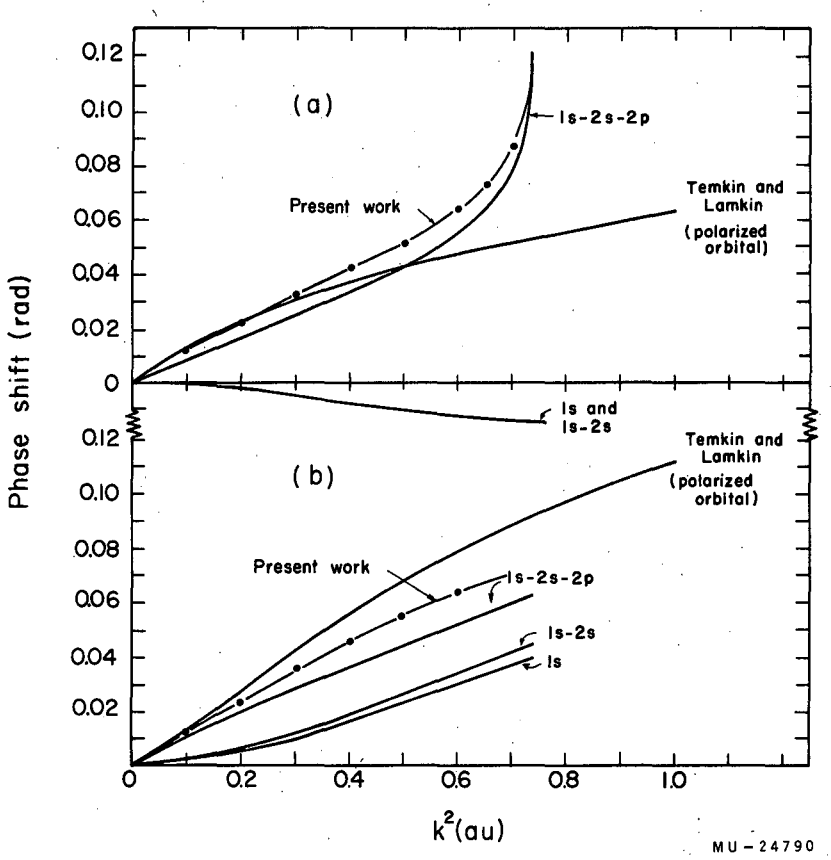


Fig. 5(a). The singlet D phase shift as a function of k^2, as given by various calculations.
(b). The triplet D phase shift as a function of k^2, as given by various calculations.

For $L > 0$ and small values of k, O'Malley et al.[23] have given an approximate expression for partial-wave phase shifts:

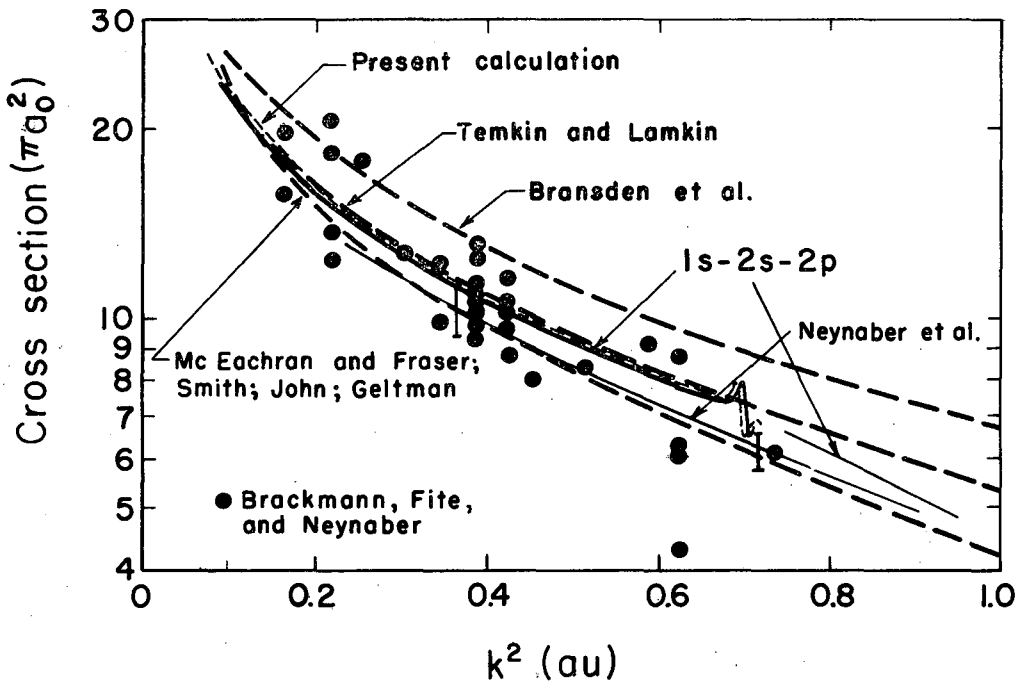
$$\tan \delta_L = \frac{\pi\alpha}{(2L+3)(2L+1)(2L-1)} k^2 + \cdots \quad . \qquad (4\text{-}6)$$

The polarizability α is equal to 4.5 in our case. The above formula yields for F-wave phase-shift values $\delta_3 = 0.00448$, 0.01792, 0.03136; for energies, $k^2 = 0.1$, 0.4, 0.7, respectively. A comparison with our results in Table I shows that they agree quite well indeed, differing only from 5 to 20%. Thus Eq. (4-6) can be used to give good approximate values for all higher-order phase shifts in the energy range in which we are interested. We also note that the magnitude of these higher-order phase shifts becomes so small that they will not contribute much to the total cross section.

E. Comparison with Experiment

In Fig. 6 we compare our result for the total cross section with the experimental results of Brackmann et al.[5] and with those of Neynaber et al.[26] We also plotted the theoretical calculations of McEachran et al.,[27] John,[23] Geltman,[27] Temkin and Lamkin,[24] Burke and Schey,[21] and Brunsden et al.[6] The large scatter of experimental points of Brackmann et al.[5] is due to the uncertainties in the electron beam energies. Various theoretical calculations do fall in the general region of the experimental points but no preference can be made with the present data.

In Fig. 7 the experimental results of Gilbody et al.[28] are compared with our result and with other theoretical predictions. Again the experimental result is such that no preference can be made among theoretical predictions, which yield angular distributions generally smooth and similar except at small scattering angles. Thus a more refined experiment is highly desirable. A spin-flip experiment[29] may yield even more information since it will predict a larger angular variation.



MU-24792

Fig. 6. Total cross section as a function of k^2, as given by various calculations.

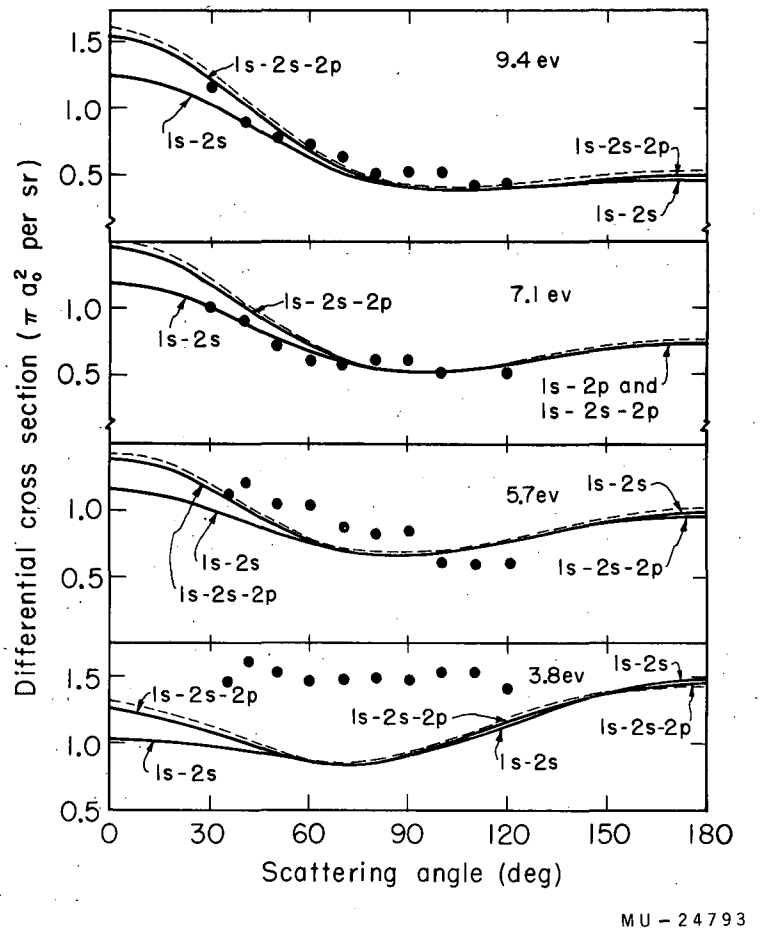


Fig. 7. Differential cross sections (dashed curves indicate present calculations).

V. CONCLUSION

From the results of our investigation, we draw the following conclusions in this final section. Particular attention is given to the range of importance of various physical effects in the atomic-scattering process and to the generalized optical-potential method as a general approach in the calculation of atomic-collision problems.

(a) The results and analysis in Sec. IV show that for S-wave scattering the short-range interelectron correlation effect is of major importance throughout the entire energy range $0 < k^2 < 0.75$. Except very near zero energy ($k^2 < 0.05$), the long-range polarization potential plays only a relatively minor role. The singlet case and the triplet case yield quite different results, which indicates the large overlapping between the incoming- and the orbital-electron wave functions. This shows the importance of taking explicit account of the Pauli principle. The effect of the long-range polarization force becomes comparable to that due to short-range correlations in the case of P-wave scattering. It is here that the results become most uncertain, and various approximations yield widely differing phase shifts.

For D waves, the long-range polarization force is very important in the scattering process while the influence of short-range correlation becomes smaller. For F(L = 3) and other higher partial waves, the long-range force becomes singularly dominant, and the centrifugal barrier pushes the incoming-electron wave function so far out that the exchange effect and the short-range correlations become negligibly small. The phase shifts have become very small and the approximate formula [Eq. (4-6)] serves as a good estimate for the phase shifts. Since different atoms are approximately of the same size, we expect the above conclusions to be quite general and of possible application in other atomic scatterings.

(b) In atomic-scattering problems most theoretical calculations assume either that the atom is completely polarized by the incoming particle (the adiabatic approximation), or that the atom remains completely unperturbed throughout the scattering (the static approximation or the Born approximation). One might wonder whether the results

from these two approaches might be useful in serving as two "bounds" for the more correct result since the adiabatic approximation over-estimates the attractive long-range polarization force while the static approximation totally neglects it.

The results for electron-hydrogen atom scattering seem to support this view. It is seen to be generally true not only for the total cross sections but also for each partial wave as well.

(c) At energies slightly below the second quantum level excitation, we found resonance-type effects in various phase shifts, similar to those found by Burke and Schey in the (1s-2s-2p) approximation.[21] These resonance-type effects are characterized by extremely narrow width and seem to exist in nearly all angular-momentum and spin states, with the effect occurring at slightly higher energies for higher partial waves. One usually would expect resonance to occur when the total energy of the scattering system is near an eigenenergy of the entire system in a bound state. This does not seem to be the case here since we know that the negative hydrogen ion has only one bound state,[30] with total energy $E = -0.5277$ (≈ -14.460 eV), while our resonance effects occur in the region $k^2 = 0.70$ to 0.75 or for total energy $-0.15 < E < -0.125$.

We suspect that these resonance phenomena may actually be spurious and only arise mathematically when solving a <u>finite</u> set of coupled equations. Indeed it may well be due, as suggested by Massey,[31] to the fact that in the close-coupled equations the energy in one closed channel is at an eigenvalue for motion in that channel uncoupled from the rest channels. That is, resonance-type effects will occur when the negative energy E_n for closed channel n in Eq. (2A-12) is such that there exists a bound state ϕ_n satisfying the Schrödinger equation

$$(E_n - K - V_{nn})\,\phi_n = 0. \qquad (5\text{-}1)$$

To see this, take the close-coupling equations of two states, Eq. (2A-12). The wave function ϕ_0 of the incoming particle in atomic channel Φ_0 satisfies an effective Schrödinger equation:

$$\left[E_0 - K - \left(V_{00} + V_{0n} \frac{1}{E_n - K - V_{nn}} V_{n0}\right)\right] \phi_0(x) = 0. \qquad (5\text{-}2)$$

The second term in the potential is then energy-dependent through the operator K and E_n, which is, by definition, $E_n = E - \epsilon_n = k^2 + (\epsilon_0 - \epsilon_n)$. When Eq. (5-1) is satisfied, the potential is infinite and hence gives rise to the "resonance" effect.

When more than one bound state is possible for Eq. (5-1), there will be "resonances" at energies corresponding to each eigenenergy of those bound states. Also, when a number of closed channels are present in the close-coupled equations, the resonance effect will occur whenever condition (5-1) is satisfied for any one of the closed channels; i.e., Eq. (5-1) may be generalized to a matrix equation, uncoupled from the elastic channel.

The above illustration did not take into account the effects of exchange and other complications in our case, but our result is qualitatively in general agreement with the conjecture, and no violation of its consequences is found. The conjecture states that the resonance effect occurs only when some state in the close-coupling is closed; the existence of a bound state in Eq. (5-1) implies that the potential V_{nn} must be attractive overall. Both conditions are satisfied in our case, where the closed channels are 2s or 2p states. If more than one bound state exists for Eq. (5-1) we expect to observe more than one resonance. In particular, we expect that the binding energy E_n is less for higher angular-momentum bound states, so the resonance energy k^2 for higher partial waves—if the resonance does occur—should be correspondingly higher, again in agreement with our result. Furthermore, the $\mathcal{V}_{2s,2s}$ in our calculation has an additional attractive polarization term of $-10.52/r^4$ as compared with the similar calculation in Burke and Schey's (1s-2s-2p) close-coupling approximation.[21] This should increase the binding energy $|E_{2s}|$ for the "bound state" ϕ_{2s} in Eq. (5-1) and, by Massey's conjecture, should lower the resonance energy. Again this agrees with calculations.

For the singlet S-wave phase shift we obtain the resonance energy $k^2_{res} = 0.700$ (9.51 eV), while the (1s-2s-2p) approximation gives $k^2_{res} = 0.707$ (9.61 eV). Following through with the conjecture, this means a shift of eigen binding energy from -0.050 to -0.043. The fact that the additional long-range force did not change the resonance energy very much seems to indicate that the ϕ_{2s} bound state does not arise because of the long-range force. Of course in some cases the additional long-range force may create a bound state which would not exist otherwise. The bound state thus created would be very loosely bound, and the corresponding resonance would then occur very near the threshold of that closed channel.

As we include more states in the close-coupling approximation, we expect a more singular behavior in the effective potential; they tend to be narrower and average out. Recently Temkin and Pohle[32] did a careful calculation on the electron-hydrogen phase shifts just below the inelastic threshold by the "nonadiabatic method." Actually their calculation is essentially a close-coupling calculation with all atomic S states and P states. They also found a very narrow resonance in the phase shift just below the second quantum level, but at about $k^2 = 0.747$ (10.17 eV). Thus the resonance behavior in phase shifts may really be an inherent characteristic of the eigenfunction expansion approach and will vanish only when we include all atomic states and solve the problem exactly.

We conclude these plausibility arguments by pointing out two other consequences which may be used to further check the conjecture. First, in positron-hydrogen scattering, the close-coupling approximation calculation should yield no such resonance since the potentials V_{nn} are not attractive and therefore the condition for a bound state in Eq. (5-1) does not exist. Second, in electron-hydrogen scattering, if we close-couple the 1s state with a much higher bound state, say 20s, the phase shift should exhibit a resonance effect at a much lower k^2 value since the field V_{nn} would be more attractive and the $|E_n|$ in Eq. (5-1) would be correspondingly higher. As n increases (still remaining bound), we expect the "resonance energy" k^2 to approach zero.

Of course, the question as to the existence of these resonance effects must ultimately be settled by experimental verification. The extremely narrow width of the singlet S-wave resonance indicates the need of an electron resolution much less than 0.05 eV.

(d) We now turn to the problem of the close-coupling scheme. In many theoretical works,[21] remarks have often been made on the importance of the "close-coupling" between two particular states in a reaction process, such as the importance of the 2s-2p coupling for 1s to 2s or 1s to 2p transition rates in a (1s-2s-2p) close-coupling approximation calculation. This, we feel, can sometimes become misleading; and not much physical understanding of the scattering process can be gained from discussion of this kind. Rather, we should talk about the entire close-coupling scheme in the calculation, since it means—in the usual eigenfunction expansion form—that we are limiting the distortion of the atom as a linear combination of those atomic states in the close-coupling schemes only.

We should like to emphasize this point: good results can not be obtained if the form of the trial wave function does not provide adequate allowance for the various effects in the scattering process. Since the bound wave functions of atomic hydrogen have definite symmetries, and radially are in general similar and smooth-varying near the origin, it simply becomes inadequate for a limited number of these hydrogen wave functions to simulate the highly distorted atom when the incoming particle gets near or inside the atom. Thus we feel that the usual eigenfunction expansion approach would be inherently a poor way to allow for such distortion and it is not surprising that when the short-range correlation effect is important, the usual close-coupling method gives poor results and converges slowly. A better allowance for such short-range distortion effect can be obtained only if we include, in the expansion, functions for the atomic electron that are more varying near the origin. The Sturmian functions used by Rotenberg,[9A] for example, would be suitable in this respect as an alternative expansion basis.

It has been noted that in the calculation of electron-hydrogen scattering the triplet results are consistently much better than the corresponding singlet results. Take, for instance, the simplest approximation of the static exchange calculation; i.e., $\psi^{\pm}(r_1, r_2) = \phi_0(r_1)\Phi_0(r_2) \pm \phi_0(r_2)\Phi_0(r_1)$. The triplet results in this approximation agree remarkably well with those of the best calculations, and the small corrections between them are more due to the long-range polarization force than to the short-range correlations. On the other hand, the singlet calculations in this case often yield quantitatively and sometimes even qualitatively different results from better calculations. Moreover, the singlet results improve only slowly as we increase the close-coupled states in the scheme, as one readily sees in the singlet S-wave case. It is here that the eigenfunction expansion approach of uncorrelated product wave functions becomes inherently ineffective, and one often resorts to introducing parameters such as the interelectron distance $\underset{\sim}{r}_{12} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$ explicitly into the trial wave function (thus rendering it non-separable), as is done in the variational calculations by Schwartz.[9]

The reason for the difference between the singlet and the triplet results lies in the fact that the Pauli effect and the Coulomb effect are additive in the triplet case while they are probably opposite in the singlet case. That is, the spatial antisymmetrization in the triplet case explicitly demands, irrespective of any approximation, that the trial wave function vanishes for $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$ (Fermi hole). This implies a repulsive effect similar to the mutual Coulomb repulsion between electrons. On the other hand, the Pauli effect in the singlet case is probably attractive, which is opposite to the effect of electron Coulomb repulsion. The poor results from the singlet calculations might very well be due to the fact that the usual singlet trial wave functions in the close-coupling approximation, while they do have the required symmetry and the simple separable product-type form, do not provide an explicit and adequate allowance for the most important part of the short-range correlation effect, the effect of Coulomb repulsion between electrons.

The success of the triplet calculations has led us to believe that the introduction of a spatially antisymmetrized factor in the trial wave function is a good way to account for the Coulomb effect while retaining the separable product-type form that characterizes the eigenfunction expansion approach. Thus as an example, we venture to suggest here—although with certain reservations—an alternative expansion form for the singlet wave function. Instead of the usual static exchange approximation, the singlet wave function in our modified expansion form may be:

$$\begin{aligned}
\psi^{+}(r_1, r_2) = \frac{1}{c}&\left[\phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) + \phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\right] \\
&\times\left[\phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) - c\,\phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\right] \\
&\times\left[c\phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) - \phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\right] \\
&= \left[\phi_0(r_1)\,\Phi_0(r_2) + \phi_0(r_2)\,\Phi_0(r_1)\right] \\
&- \left(c - 1 + \frac{1}{c}\right)\left[\phi_0^{2/3}(r_1)\,\Phi_0^{1/3}(r_1)\,\phi_0^{1/3}(r_2)\,\Phi_0^{2/3}(r_2)\right. \\
&\left. + \phi_0^{2/3}(r_2)\,\Phi_0^{1/3}(r_2)\,\phi_0^{1/3}(r_1)\,\Phi_0^{2/3}(r_1)\right]. \qquad (5\text{-}3)
\end{aligned}$$

It is easy to see that the modified static exchange approximation is symmetric under the exchange of particles 1 and 2. In addition, the almost antisymmetrized factors in the wave function insures that, for values of c near 1, the wave function will have a dip as $\underset{\sim}{r}_1$ approaches $\underset{\sim}{r}_2$; and for $c = 1$ it vanishes for $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$. The value of c can perhaps be determined variationally but we expect $c = 1$ might be adequate. In form, it differs from the ordinary singlet static exchange wave function by the last two terms in Eq. (5-3). The asymptotic boundary conditions of ϕ_0 in this modified expansion are the same as before. For $r_1 \to \infty$, $\psi^{(+)}$ goes to $\phi_0(r_1)\,\Phi_0(r_2)$ and so again we have the simple relation between the function ϕ_0 and the scattering cross section.

It might be argued that the modified expansion form is no longer a one-state approximation, but this is a deviation no more than the ordinary static exchange approximation is a deviation from a one-state approximation. The major objection would be that the resulting equation is nonlinear, which may yield some surprising properties not contained in the physics of the problem. In Appendix E we derived the resulting equation to be solved when we use this modified static exchange approximation. The labor involved in the numerical computation of the resulting equation is not much greater than in calculating the ordinary static exchange approximation, and is certainly much less than that of a (1s-2s) close-coupling approximation with exchange.

(e) In Subsec. I-B, we give a general physical picture of the atomic-scattering process where we mentioned the possible breakdown of adiabatic condition at distances much greater than the atomic dimension. This effect we termed the long-range nonadiabatic effect. It is of interest to see whether in our electron-hydrogen case this nonadiabatic effect does become significant at distances large enough so that it may be separated from the short-range correlation effect.

To this end, we expand the propagator $1/a^+$ in the adiabatic approximation limit:

$$\frac{1}{a^+} = \frac{1}{d^+} + \frac{1}{d^+}(E_{p_0} - K - V)\frac{1}{d^+} + \cdots \quad . \tag{5-4}$$

When this is substituted into the second-order term in the optical potential [Eq. (2B-2)] for electron-hydrogen elastic scattering, the first term on the right in Eq. (5-4), $1/d^+$, yields the familiar adiabatic polarization potential,[1] which at large distance is $-2.25/r^4$. The second term on the right in Eq. (5-4) contains the first nonadiabatic correction. In Appendix F this first-order nonadiabatic correction is evaluated. Neglecting the exponentially decreasing terms, we obtain

$$\mathcal{V}_{NA} = -\Bigg[\frac{1}{r} + (8 - 3\ln 2 + 2\ln^2 2)\frac{1}{r^3}$$

$$+ e^{2r}\,\mathcal{E}i(-2r)\left(1 - \frac{4}{r} + \frac{11}{2r^2} - \frac{5}{2r^3} - \frac{3}{2r^4}\right)$$

$$+ e^{-2r}\,\mathcal{E}i(+2r)\left(-1 - \frac{4}{r} - \frac{11}{2r^2} - \frac{5}{2r^3} + \frac{3}{2r^4}\right)$$

$$+ \frac{2}{r^3}\,\mathcal{E}i(-2r)\,\mathcal{E}i(+2r)$$

$$+ \mathcal{J}\Bigg]\frac{\partial}{\partial r}\,; \qquad (5\text{-}5)$$

where $\mathcal{J}$ contains nonintegrable terms,

$$\mathcal{J} = -\frac{1}{r^2}\left(\frac{1}{r} - 1\right)\left[\frac{1}{r}S_2 - S_0\left(\frac{1}{r} - \frac{2}{r^2} + \frac{2}{r^3}\right)\right]$$

$$- \frac{1}{r^2}\left(\frac{1}{r} + 1\right)\left[\left(\frac{1}{r} + \frac{2}{r^2} + \frac{2}{r^3}\right)T_0 - \frac{1}{r}T_2\right],$$

where

$$S_n = \int_1^\infty d\lambda\,\lambda^n\left|\ln(1+\lambda)\right|^2 e^{-r(\lambda-1)},$$

$$T_n = \int_{-1}^{+1} d\mu\, e^{-r(\mu+1)}\,\mu^n\left|\ln(1-\mu)\right|^2 .$$

We note that this first-order nonadiabatic correction term is linearly proportional to $\partial/\partial r$, or linearly velocity-dependent. Thus its contribution goes to zero linearly as the particle's radial velocity approaches zero, in keeping with the definition of adiabatic correction. For its behavior at large distances, we expand the expression (5-5)

in powers of $1/r$ and the leading term yields

$$\lim_{r\to\infty} \mathcal{V}_{NA} = -10.75 \cdot \frac{1}{r^5} \frac{\partial}{\partial r} , \tag{5-6}$$

in agreement with the estimate of Mittleman.[13A] Thus we may write the optical potential at large distance as

$$\mathcal{V} = -2.25/r^4 - \frac{10.75}{r^5} \frac{\partial}{\partial r} . \tag{5-7}$$

To find the influence of the nonadiabatic term on the scattered particle, we do as follows. For very-low-energy scattering, we assume the electron has zero energy at infinity and falls into the potential of Eq. (5-7). The gradient $(-\partial/\partial r)$ is set equal to the incoming-electron momentum, and by energy conservation this potential term must equal the kinetic energy acquired, $p^2/2$. Thus the momentum of the electron at distance r is given by the relation

$$p^2/2 = 2.25/r^4 - (10.75/r^5)p. \tag{5-8}$$

The corresponding expression for adiabatic potential alone is

$$p_0^2/2 = 2.25/r^4. \tag{5-9}$$

The ratio p/p_0 is evaluated for various values of r and is presented in Table IV. It is seen that the ratio p/p_0 does not deviate much from unity for $r > 3$. Thus we conclude that for near-zero energy in electron-hydrogen scattering, the whole nonadiabatic effect at large distance is quite small.

Table IV. Evaluation of ratio p/p_0 at various values of r.[a]

r	p/p_0
20	0.999
10	0.995
4.6	0.951
3.7	0.904
2.72	0.779
2.15	0.623
1.71	0.40

[a] $p/p_0 = -5.067/r^3 + (1 + 25.7/r^6)^{1/2}$.

At higher energies the above will not be valid and we look at the ratio of the nonadiabatic correction term to the adiabatic potential term. For an initial momentum of 0.75 (i.e., incoming-electron energy = 7.65 eV), the ratio is approximately $(10.75 \cdot r^{-5} \times 0.75/2.25 \cdot r^{-4}) = 3.58/r$. Thus it is already 35.8% at $r = 10$ and is 71.6% at $r = 5$. Therefore in this energy range the nonadiabatic effect will not be small and cannot be neglected. However, in our calculation we do partially include the nonadiabatic correction by the close-coupling of (1s-2s-2p) states. The contribution of 2p states to the long-range nonadiabatic correction term has also been evaluated in Appendix F and is found to be $-7.9(1/r^5)(\partial/\partial r)$, or 73.5% of the total. It is reassuring to know that this large portion of the nonadiabatic correction has been implicitly included in our calculation.

(f) Finally, after having presented the formalism of the generalized optical-potential method and having applied it to the elastic scattering of electrons by hydrogen atoms; it is only appropriate to give here an overall evaluation of the usefulness of the method in treating general atomic-scattering problems. First of all, the generalized optical-potential method retains the form of the usual eigenfunction expansion approach, making it particularly suitable for the calculations of reaction cross sections, and also partially taking the nonadiabatic effect into account through the differential equations. Of course the special feature of the generalized optical-potential method in practical applications is that it will always give the correct long-range polarization potential. That the influence of the long-range induced potential is of paramount importance in low-energy atomic scattering cannot be too strongly emphasized. In the electron-oxygen-atom scattering, as Temkin[10] pointed out, the polarization potential decreases the theoretical zero-energy exchange approximation cross section by a factor of 8 and by a factor of 2 at energies of 10 eV. Both These values seem to be confirmed by experiment.

Thus our choice of the application to the electron-hydrogen case was not meant to show to the fullest the advantages (and the virtues) of our method, since we have calculated the elastic scattering only, and

the 2p atomic states in our close-coupling scheme have an implicit and exceptionally large contribution to the long-range polarization potential, 66%. A close-coupling scheme with only 1s and 2s atomic states would certainly demonstrate the advantages of our method over the conventional close-coupling approximation in a more impressive manner. Even so, our calculation shows that the addition of the other 34% of the correct long-range potential by our method still did alter the higher partial phase shifts significantly.

As is characteristic of the eigenfunction expansion approach, our method is less successful in singlet low-angular-momentum states where the short-range correlation effect is important. The excellent results from the rather crude approximations in the triplet case indicate that the allowance for mutual repulsion, or the Coulomb hole, constitutes the major effect of short-range correlations. It also led us to propose an alternative expansion form for the singlet case. It is our belief that this type of modified singlet wave-function expansion, or a more suitable expansion basis (such as the Sturmian functions), should remedy and compliment the generalized optical-potential method, making it the most versatile and practical theoretical method in the treatment of atomic-scattering problems.

ACKNOWLEDGMENTS

I want to express my deep gratitude: to Dr. Marvin H. Mittleman for his guidance, encouragement, and patience throughout the course of this work; to Professor K. M. Watson who first stimulated my interest in this field; and to Dr. Philip G. Burke for his generous help with the computer program. Enlightening discussions with Professor Charles Schwartz and Dr. Hugh P. Kelly are also gratefully acknowledged.

This work was done under the auspices of the U. S. Atomic Energy Commission.

APPENDICES

A. Proof That a^+ and Π_N Commute

We want to prove that a^+ and Π_N commute. The projection operator Π_N is defined to project the target wave function onto the N atomic channels $\sum_i^N \Phi_i(z)$, but it has no effect on the scattered-particle coordinate x. We thus may write explicitly

$$\Pi_N = \delta(x - x') \sum_i^N \Phi_i(z)\Phi_i(z').$$

Now $a^+ = E - H - K + i\eta$. To the target wave functions $\Phi_i(z)$'s, the $(E - K + i\eta)$ in a^+ are effectively c numbers while H is just the eigen-Hamiltonian for the Φ's. Thus

$$\left[\Pi_N, a^+\right] = 0.$$

B. Reduction of the Partial-Wave Treatment to Radial Equations

The algebraic problem of obtaining explicit radial equations from the partial-wave treatment for electron-hydrogen-atom collisions was first given by Percival and Seaton.[18] We give here the pertinent quantites of the radical equations which we numerically solved on an IBM 7090 computer.

Let the hydrogen atom wave functions be denoted by,

$$\Phi_{n\ell_1 m_1}(r) = \frac{1}{r} R_{n\ell_1}(r)\, Y_{\ell_1 m_1}(\hat{r}), \qquad \text{(B-1)}$$

where $R_{n\ell}$ is a normalized radial function, and $Y_{\ell m}$ is a normalized spherical harmonic. For our scattering problem the total wave function can be expanded in explicit antisymmetrized form:

$$\psi_c(\underset{\sim}{r}_1\sigma_1, \underset{\sim}{r}_2\sigma_2) = \frac{1}{\sqrt{2}} \sum_{\Gamma} \left[\psi_\Gamma(\underset{\sim}{r}_1\sigma_1, \hat{r}_2\sigma_2) \frac{F_\Gamma(r_2)}{r_2} - \psi_\Gamma(\underset{\sim}{r}_2\sigma_2, \hat{r}_1\sigma_1) \frac{F_\Gamma(r_1)}{r_1} \right] . \qquad \text{(B-2)}$$

The representation is labeled $\Gamma = (nk_n\ell_1\ell_2LM_LSM_s)$ where the total angular momentum L and the total spin S of the system are separately conserved in the scattering process. The n and ℓ_1 are the principal and the angular-momentum quantum numbers, respectively, of the atomic electron; the ℓ_2 and k_n are the orbital angular momentum and the wave number, respectively, of the scattered electron. The sum over Γ in Eq. (B-2) includes the close-coupled states $(n\ell_1)$ of the hydrogen atom as well as the values of ℓ_2 consistent with the given L.

The exact generalized optical-potential solution ψ_c satisfies the Kohn-Hulthén variational principle:

$$\delta\left[\int \psi_c^{LS*}(\nu) \left(\mathcal{H} - E\right) \psi_c^{LS}(\nu') \, d\tau_1 d\tau_2 - \frac{1}{2} A_{LS}^2 R_{\nu\nu'}^{LS} \right] = 0, \qquad \text{(B-3)}$$

where $\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \mathcal{V}$.

The $F_\Gamma(\nu)$ from $\psi_c^{LS}(\nu)$ has the boundary conditions

$$\left.\begin{aligned} \lim_{r\to\infty} F_{\nu'}^{LS}(\nu; r) &= \frac{A_{LS}}{k_{n'}^2} \left[\delta_{\nu\nu'} \sin(k_{n'} r - \tfrac{1}{2}\ell'_2\pi) + R_{\nu\nu'}^{LS} \cos(k_{n'} r - \tfrac{1}{2}\ell'_2\pi) \right], \\ &\quad \text{if } \nu' \text{ channel is energetically open} \\ &= 0, \text{ if } \nu' \text{ is closed} \end{aligned}\right\} \qquad \text{(B-4)}$$

and $F^{LS}_{\nu'}(\nu;0) = 0$ for all channels. Here we write Γ explicitly as $LS\nu$, where ν denotes $n_1\ell_1\ell_2$.

Carrying out the manipulations for (B-3) with boundary conditions (B-4), we find $F^{LS}_{\nu}(r)$ must satisfy a set of close-coupled equations

$$\left[\frac{d^2}{dr^2} - \frac{\ell_2(\ell_2+1)}{r^2} + k^2\right] F^{LS}_{\nu}(r) = \sum_{\nu'} 2\left(V^{L}_{\nu\nu'} - W^{LS}_{\nu\nu'}\right) F^{LS}_{\nu'}(r). \tag{B-5}$$

The symbols in (B-5) are:

$$\frac{1}{2} k_n^2 = (E - \epsilon_n), \tag{B-6}$$

$$V^{L}_{\nu\nu'}(r) = -\frac{1}{r}\delta_{\nu\nu'} + \sum_{\lambda} f_\lambda(\ell_1\ell_2\ell'_1\ell'_2; L) y_\lambda(P_{n\ell_1} P_{n'\ell'_1} | r)$$

$$+ \mathcal{V}^{(2)}_{\nu\nu'}, \tag{B-7}$$

$$W^{LS}_{\nu\nu'} F^{LS}_{\nu'}(r) = (-1)^{1-S} \sum_{\lambda} g_\lambda(\ell_1\ell_2\ell'_1\ell'_2; L)$$

$$\times\left[\delta_{\lambda 0}(\epsilon_n - \epsilon_{n'} - E)\Delta(P_{n\ell_1} F_{\nu'}) + y_\lambda(P_{n\ell_1} F_{\nu'} | r)\right] P_{n'\ell'_1}(r), \tag{B-8}$$

where

$$\Delta(A, B) = \int_0^\infty A(r)\, B(r)\, dr, \tag{B-9}$$

$$y_\lambda(AB|r) = r^{-(\lambda+1)} \int_0^r A(r')\, B(r')\, r'^{\lambda}\, dr' + r^{\lambda} \int_r^\infty A(r')\, B(r')\, r'^{-(\lambda+1)} dr', \tag{B-10}$$

$$f_\lambda(\ell_1\ell_2\ell_1'\ell_2'; L) = (\ell_1\ell_2 L \,|\, P_\lambda(\hat{r}_1 \cdot \hat{r}_2) \,|\, \ell_1'\ell_2' L), \tag{B-11}$$

$$g_\lambda(\ell_1\ell_2\ell_1'\ell_2'; L) = (-)^{\ell_1+\ell_2-L} (\ell_1\ell_2 L \,|\, p_\lambda(\hat{r}_1 \cdot \hat{r}_2) \,|\, \ell_2'\ell_1' L). \tag{B-12}$$

The $P_\lambda(x)$ is the familiar Legendre polynomial and the $\mathcal{V}^{(2)}_{\nu\nu'}$ in (B-7) is as given in Subsec. III-B.

When only the elastic channel is open, $R^{LS}_{\nu\nu'}$ in (B-4) reduces to a single element $\tan\delta^{LS}$, where δ^{LS} is the phase shift for the given state of L and S. The elastoc-scattering differential cross section in either spin state is then

$$\sigma_S(\theta) = \left| \frac{1}{2ik} \sum_L (2L+1) \left[\exp(2i\delta^{LS}) - 1 \right] P_L(\cos\theta) \right|^2, \tag{B-13}$$

and the total cross section is

$$S = \frac{4\pi}{k^2} \sum_L (2L+1) \sin^2\delta^{LS} . \tag{B-14}$$

For an unpolarized electron beam the total cross section is

$$\sigma^{total} = \frac{1}{4} \left| \sigma_{S=0} + 3\sigma_{S=1} \right| . \tag{B-15}$$

C. Numerical Procedure for Solving the Set of Coupled Integral-Differential Equations

Here we describe briefly the general procedure for solving the set of coupled integral-differential radial equations.

The set of equations can be written as

$$\frac{d^2F_i(r)}{dr^2} = \sum_j V_{ij}(r)\, F_j(r) + \sum \int_0^\infty K_{ij}(r_1 r')\, F_j(r')\, dr', \tag{C-1}$$

where ij = 1, $\cdots$, n; n being the number of radial wave functions consistent with our close-coupling scheme. The $V_{ij}(r)$'s represent the

direct potentials, the energy, and the centrifugal barrier; $K_{ij}(r, r')$ represents the exchange potentials. For a suitably chosen r_a we may write $V_{ij}(r)$ as a finite sum of the inverse power of r for $r > r_a$; we may also consider that the exchange kernel $K_{ij}(r, r')$ vanishes for r or $r' \geqslant r_a$.

Let there be n_a energetically open channels and n_b closed channels, $n_a + n_b = n$. Because of the boundary conditions at infinity, for the region $r > r_a$ the general solution is determined by $(2n_a + n_b)$ or $(n + n_a)$ parameters—two arbitrary parameters for each open channel and one for each closed channel. The boundary condition at origin requires $F_i(0) = 0$ for all i, thus a solution for (C-1) is determined by n arbitrary parameters.

To determine $F_i(r)$ for $r_a \geqslant r \geqslant 0$, we cannot take straightforward numerical integration out from the origin. This is due to the fact that in n_b closed channels the increasing exponential component of the solution would grow to such an extent that the exponentially decreasing term—the part that satisfies the boundary condition at infinity— would be completely overwhelmed and lost. Nor can we start from $r = r_a$ and integrate inward, since this would produce irregular solutions at small r and would not vanish at origin. To circumvent both difficulties, we take the compromising way by choosing an adjustable middle point r_0. We shall solve the n linearly independent inner solutions for $0 < r < r_0$ by outward integration from $r = 0$. We also solve the $n + n_a$ linearly independent outer solution for $r_a > r > r_0$ by integrating from $r = r_a$ inward.

The interactive procedure to obtain a continuous solution is as follows. First we set the kernel K to zero; the resulting homogeneous equations will yield n set inner solutions $F_i^{(0)j}(r)$ for $j = 1, \cdots, n$ in the region $0 < r < r_0$; and for $j = 1, \cdots, n + n_a$ in the region $r_0 < r < r_a$. The superscript in parentheses indicates the iteration number. The unique continuous solution is obtained by linearly combining those solutions and demanding that the function and its derivative be continuous at $r = r_0$. Let this continuous solution be denoted as $F_i^{(0)}$, the zeroth-order continuous solution.

Now we use $F_i^{(0)}$ to evaluate the exchange term $\int KF_i dr'$, and solve the resulting inhomogeneous equation once more to obtain the first-order inner solution $f_i^{(1)}(r)$ and outer solution $g_i^{(1)}(r)$. Again they may not be matched at $r = r_0$, so we again add linear combinations of the zero-order homogeneous solutions $F^{(0)j}$ and $G^{(0)j}$ to it and demand continuity at $r = r_0$. This gives us the first-order continuous solution $F_i^{(1)}(r)$. This is, then, again used to evaluate the exchange term, which in turn is used to find $f_i^{(2)}$ and $g_i^{(2)}$, etc.

Thus we have

$$F_i^{(n)}(r) = f_i^{(n)}(r) + \sum_{j=1}^{n} a_j^{(n)} F_i^{(0)j}(r) \quad 0 \leq r \leq r_0$$

$$= g_i^{(n)}(r) + \sum_{j=1}^{n+n_a} b_j^{(n)} G_i^{(0)j}(r) \quad r_0 \leq r \leq r_a$$

$$i = 1, 2, \cdots, n. \tag{C-2}$$

The coefficients $a_j^{(n)}$ and $b_j^{(n)}$ are determined, of course, by the continuity condition at $r = r_0$, or more explicitly

$$f_i^{(n)}(r_0) + \sum_j a_j^{(n)} F_i^{(0)j}(r_0) = g_i^{(n)}(r_0) + \sum_j b_j^{(n)} G_i^{(0)j}(r_0),$$

$$\left.\frac{df_i^{(n)}(r)}{dr}\right|_{r_0} + \sum_j a_j^{(n)} \left.\frac{dF_i^{(0)j}(r)}{dr}\right|_{r_0} =$$

$$\sum_j b_j^{(n)} \left.\frac{dG_i^{(0)j}(r)}{dr}\right|_{r_0} + \left.\frac{dg_i^{(n)}(r)}{dr}\right|_{r_0}. \tag{C-3}$$

The parameters a's and b's (totalling $2n + n_a$) are thus related by those 2n equations. To speed the convergence we use the remaining n_a degrees of freedom by imposing n_a integral conditions, which amounts to a normalization procedure on the first n_a functions of $F_i^{(n)}$. That is, we impose

$$\int_0^{r_c} F_i^{(n)}(r)\, dr = c_i, \quad i = 1, \cdots, n_a, \tag{C-4}$$

where c_i's and r_c's are chosen arbitrarily. In general $0 < r_c < r_0$, but r_c may be bigger or smaller than r_a.

Thus the iteration goes on until convergence is obtained; i.e., $F_i^{(n)}$ and $F_i^{(n+1)}$ are equal within some predetermined amount. The Runge-Kutta integration method is used to solve the equivalent set of difference equations. For our calculation $r_a = 28$ au, $r_c = 2$ to 4 au, and $r_0 = 5$ or 10 au. The basic grid interval is 0.1 au and generally gives the phase shift correct to about four decimal places.

D. Proof of Relaxation of Restriction on ϕ's in Eq. (3B-16)

The generalized optical wave function is written as

$$\psi_c^{\pm} = \sum_n^N (1 \pm P_{12})\, \phi_n(1)\, \Phi_n(2), \tag{D-1}$$

and the projection operators π_n used in defining $\psi_c^{\pm}$ place the additional restriction that the scattered-particle wave function ϕ_n's be orthogonal to atomic wave functions Φ_m's for $m < n$ in the ordering scheme. That is,

$$\left\langle \phi_n \,\middle|\, \Phi_m \right\rangle = 0 \qquad \text{for } n > m. \tag{D-2}$$

Because of the spatial symmetrization or antisymmetrization operator $(1 \pm P_{12})$ and the fact that we are summing up all N states together in $\psi_c^{\pm}$, and because we demand that the N states be the

lowest in our ordering scheme, the restriction (D-2) can actually be relaxed in Eq. (D-1).

To prove this we need only to show that the expression of Eq. (D-1) is not unique but may be rewritten as

$$\psi_c^{\pm} = \sum_{i}^{N} (1 \pm P_{12}) \nu_n(1) \, \Phi_n(2), \tag{D-3}$$

where the restriction (D-2) does not apply to the ν's.

To begin, we show the restriction on the ϕ's explicitly by writing

$$\phi_n(1) = F_n(1) - \sum_{m > n} C_{nm} \, \Phi_m(1), \tag{D-4}$$

where the nonzero coefficients C_{nm} are defined to be:

$$C_{nm} = \left\langle \Phi_m \middle| F_n \right\rangle \neq 0, \quad \text{for } m < n.$$

This insures the orthogonality condition (D-2) for the ϕ_n's.

Substituting Eq. (D-4) in Eq. (D-1), we get

$$\psi_c^{\pm} = \sum_{n}^{N} (1 \pm P_{12}) \left[F_n(1) - \sum_{m<n} C_{nm} \, \Phi_m(1) \right] \Phi_n(2)$$

$$= \sum_{n}^{N} (1 \pm P_{12}) \, F_n(1) \, \Phi_n(2)$$

$$- \sum_{n}^{N} (1 \pm P_{12}) \sum_{m<n}^{N} C_{nm} \, \Phi_m(1) \, \Phi_n(2). \tag{D-5}$$

We now use the identity relation

$$(1 \pm P_{12}) = (1 \pm P_{12}) \, (\pm P_{12}) \tag{D-6}$$

on the second term on the right side of Eq. (D-5), which becomes

$$\text{"2nd term"} = \sum_{n}^{N} (1 \pm P_{12})(\pm P_{12}) \left[\sum_{m<n} C_{nm} \Phi_m(1) \Phi_n(2) \right]$$

$$= \sum_{n}^{N} (1 \pm P_{12}) \left[\sum_{m<n} (\pm) C_{nm} \Phi_m(2) \Phi_n(1) \right]$$

(changing summing order)

$$= \sum_{m}^{N} \sum_{n>m} (1 \pm P_{12}) (\pm) C_{nm} \Phi_n(1) \Phi_m(2)$$

(now changing index)

$$= \sum_{n}^{N} \sum_{m>n} (1 \pm P_{12}) (\pm) C_{mn} \Phi_m(1) \Phi_n(2). \qquad \text{(D-7)}$$

Substituting Eq. (D-7) back into Eq. (D-5), we obtain

$$\psi_c^{\pm}(1c2) = \sum_{n}^{N} (1 \pm P_{12}) \left[F_n(1) \mp \sum_{m>n} C_{mn} \Phi_m(1) \right] \Phi_n(2). \qquad \text{(D-8)}$$

To equate Eq. (D-8) to Eq. (D-3), we need only to let

$$\nu_n(1) = F_n(1) \mp \sum_{m>n} C_{mn} \Phi_m(1). \qquad \text{(D-9)}$$

The ν's do not have the restriction Eq. (D-2) as the ϕ's do, since

$$\left\langle \nu_n \middle| \Phi_p \right\rangle = \left\langle F_n \mp \sum_{m>n} C_{mn} \Phi_m \middle| \Phi_p \right\rangle$$

$$= C_{pn}$$

$$\neq 0 \qquad \text{for } p < n.$$

E. The Algebraic Problem of the Modified Trial Wave Function, Eq. (E-1)

To take better account of the interelectron repulsion in the electron–hydrogen-atom scattering, we suggest to replace the usual singlet wave function in the static exchange approximation by an alternative expression

$$\begin{aligned}
\psi^{+}(r_1, r_2) = \frac{1}{c}\Big[& \phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) + \phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\Big] \\
& \times\Big[\phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) - c\,\phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\Big] \\
& \times\Big[c\phi_0^{1/3}(r_1)\,\Phi_0^{1/3}(r_2) - \phi_0^{1/3}(r_2)\,\Phi_0^{1/3}(r_1)\Big] \\
= & \Big[\phi_0(r_1)\,\Phi_0(r_2) + \phi_0(r_2)\,\Phi_0(r_1)\Big] \\
& - \left(c - 1 + \frac{1}{c}\right)\Big[\phi_0^{2/3}(r_1)\,\Phi_0^{1/3}(r_1)\,\phi_0^{1/3}(r_2)\,\Phi_0^{2/3}(r_2) \\
& + \phi_0^{2/3}(r_2)\,\Phi_0^{1/3}(r_2)\,\phi_0^{1/3}(r_1)\,\Phi_0^{2/3}(r_1)\Big] \quad . \quad \text{(E-1)}
\end{aligned}$$

This expression differs from the usual static exchange approximation by the addition of the last two terms. These two terms are short-ranged; i.e., they vanish for either r_1 or r_2 going to infinity. This alternative expression of $\psi^{+}(r_1, r_2)$ not only is symmetric under the exchange of coordinates r_1 and r_2, but also has the additional property of vanishing when $r_1 = r_2$, thus giving a natural provision for the Coulomb hole.

The Schrödinger equation for the electron–hydrogen-atom scattering is

$$\left[H_1^0 + H_2^0 + V_{12} - E\right] \psi^+(r_1, r_2) = 0, \tag{E-2}$$

where H^0 represents the Hamiltonian of the Coulomb wave function

$$H_1^0 = K_1 + V_1, \qquad H^0 \Phi_n = \epsilon_n \Phi_0 .$$

For an incoming particle of initial energy of k^2, the total energy E of the system is $E = k^2 + \epsilon_0$. Substituting Eq. (E-1) into the Schrödinger equation (E-2), premultiplying by $\phi_0(r_1)$ and integrating over the coordinate r_1, we derive an integro-differential equation for the function $F(r_2)$.

$$\left[H_2^0 + U_0 - \frac{k^2}{2}\right] F(r_2) + \left[(\epsilon_0 - k^2)\Delta(1) + J(1)\right]\phi_0(r_2)$$

$$= (c-1+\frac{1}{c}) \left\{\left[\Delta(\tfrac{1}{3}) (H_2^0 - \frac{k^2}{2}) + J(\tfrac{1}{3})\right] \phi^{1/3}(r_2) F^{2/3}(r_2)\right.$$

$$\left. + \left[\Delta(\tfrac{2}{3}) (H_2^0 - \frac{k^2}{2}) + J(\tfrac{2}{3})\right] \phi^{2/3}(r_2) F^{1/3}(r_2)\right\}, \tag{E-3}$$

where

$$U_0 = \int \phi_0^*(r_1) V_{12} \phi_0(r_1) d\underset{\sim}{r}_1 = J(0),$$

$$J(m) = \int \phi_0^*(r_1) V_{12} \phi^{(1-m)}(r_1) F^m(r_1) d\underset{\sim}{r}_1,$$

$$\Delta(m) = \int \phi_0^*(r_1) \phi^{(1-m)}(r_1) F^m(r_1) d\underset{\sim}{r}_1 .$$

The $\Delta(m)$ is a kind of generalized overlapping integral while $J(m)$ may be called a generalized exchange potential. Were we to let the terms on the right-hand side of the equality in (E-3) vanish, we obtain just the integral-differential equation for the ordinary static exchange approximation. The terms on the right-hand side of (E-3) thus come from our modified static exchange approximation.

When we use the generalized optical-potential method, the wave function $\psi^+(r_1, r_2)$ then satisfied the equation (3B-14). We then replace V_{12} in U_0 by the generalized optical potential $\mathcal{V}_{12}$. For S-wave singlet scattering, our modified static exchange approximation does not contribute to the polarization potential. We shall add the direct long-range polarization potential terms in the optical potential; the net result is the replacement $U_0 = J(0)$ by

$$U_0 = J(0) + \frac{-a}{2r^4} f(r),$$

where f(r) is some function to cut off this dipole potential at small r.

The boundary conditions for F(r) are the same as usual. For S-wave scattering,

$$F(r) \lim_{r\to\infty} = \frac{1}{rk^{1/2}} \sin(kr + \delta),$$

$$F(0) = \text{constant}.$$

F. Calculation of the First-Order Nonadiabatic Correction of the Optical Potential for Electron-Hydrogen Scattering

From Eq. (2B-2), the second-order term of the optical potential for the elastic scattering of an electron by a hydrogen atom in ground state is:

$$\mathcal{V}^{(2)} = \left\langle 0 \left| V_{12} \frac{(I - \pi_0)}{a^+} V_{12} \right| 0 \right\rangle . \qquad \text{(F-1)}$$

By using Eq. (5-4), the adiabatic expansion of $1/a^+$, $\mathcal{V}^{(2)}$ yields, along with the familiar polarization potential, the first non-adiabatic correction term $\mathcal{V}_{NA}$:

$$\mathcal{V}_{NA} = \left\langle 0 \left| V_{12} \frac{(I - \pi_0)}{d^+} (K_1 + V_1 - E_{P_0}) \frac{(I - \pi_0)}{d^+} V_{12} \right| 0 \right\rangle$$

$$= \left\langle 0 \left| F(K_1 + V_1 - E_{P_0}) F \right| 0 \right\rangle , \qquad \text{(F-2)}$$

where

$$F \left| 0 \right\rangle = \frac{(I - \pi_0)}{d^+} V_{12} \left| 0 \right\rangle$$

$$= f \left| 0 \right\rangle - \left\langle 0 \right| f \left| 0 \right\rangle \left| 0 \right\rangle . \qquad \text{(F-3)}$$

The function f has previously been solved by Dalgarno and Lynn.[33]

Now

$$\left[E_{P_0} , \quad F \right] = 0,$$

$$\left[V_{12}, \quad F \right] = 0 \quad ,$$

and

$$K_1 = -1/2 \, \nabla_1^2 , \text{ so}$$

$$K_1 \, F = (-1/2 \, \nabla_1^2) \, F$$

$$= -1/2 \, (\nabla_1^2 F) - (\underset{\sim}{\nabla}_1 F) \cdot \underset{\sim}{\nabla}_1 - (1/2) F \, \nabla_1^2 . \qquad \text{(F-4)}$$

Substituting this in Eq. (F-2), we have

$$\mathcal{V}_{NA} = \left\langle 0 \right| F \, (K_1 + V_1 - E_{P_0}) \, F \left| 0 \right\rangle$$

$$= - \left\langle 0 \right| F \, \underset{\sim}{\nabla}_1 \, F \left| 0 \right\rangle \cdot \underset{\sim}{\nabla}_1$$

$$- (1/2) \left\langle 0 \right| F \, (\nabla_1^2 F) \left| 0 \right\rangle$$

$$+ \left\langle 0 \right| F \, F \left| 0 \right\rangle \, (-\tfrac{1}{2} \nabla_1^2 + V_1 - E_{P_0}). \qquad \text{(F-5)}$$

Now

$$\nabla_1^2 \, F = \nabla_1^2 \left[\frac{(I - \pi_0)}{d^+} V_{12} \right]$$

$$= \frac{(I - \pi_0)}{d^+} (\nabla_1^2 V_{12})$$

$$= \frac{(I - \pi_0)}{d^+} \, \delta \, (\underset{\sim}{r}_1 - \underset{\sim}{r}_2).$$

This shows that the second term in Eq. (F-5) will only contribute exponentially decreasing terms, so we may drop it. The higher-order terms in the optical potential will add to the third term in Eq. (F-5) to give $\langle 0 | F \cdot F | 0 \rangle \cdot (-\frac{1}{2} \nabla_1^2 + \mathcal{V} - E_{P_0})$, which will vanish identically when operating on the scattered-particle wave function.

Finally, the first term in Eq. (F-5) contains a vector operator $\underset{\sim}{\nabla}_1$. However, from symmetry arguments, we can see that only the radial part contributes. So we finally have

$$\mathcal{V}_{NA} = -\langle 0 | F \left(\frac{\partial}{\partial r_1} F \right) | 0 \rangle \frac{\partial}{\partial r_1}$$

$$= -\Big[\langle 0 | f \left(\frac{\partial}{\partial r} f \right) | 0 \rangle \tag{F-6}$$

$$- \langle 0 | f | 0 \rangle \langle 0 | \left(\frac{\partial}{\partial r} f \right) | 0 \rangle \Big] \frac{\partial}{\partial r} .$$

Using the function f given by Delgarno and Lynn,[33] expressed in confocal elliptical coordinates, we have evaluated the above expression. The result, neglecting the exponentially decreasing terms, is as given in Eq. (5-5). It gives a leading term

$$\mathcal{V}_{NA} = -(43/4)(1/r^5) \frac{\partial}{\partial r} , \tag{F-7}$$

in agreement with the estimates of Mittleman.[13A]

The contribution of the 2P atomic states at large distances is evaluated by multipole expansion of V, which readily yields

$$\sum_{2P} -\langle 0 | V | 2P \rangle \left(\frac{1}{d_{2P}} \right)^2 \langle 2P | \left(\frac{\partial}{\partial r} V \right) | 0 \rangle \frac{\partial}{\partial r}$$

$$= \left(\frac{1}{3} \right) \left(\frac{1}{(3/8)^2} \right) \left[\int_0^\infty R_{1s}(r') r' R_{2p}(r') \frac{dr'}{r^2} \right]$$

$$\cdot (-2) \left[\int_0^\infty R_{2p}(r') r' R_{1s}(r') \frac{dr'}{r^3} \right] \left(\frac{\partial}{\partial r} \right)$$

$$= -\left(\frac{7.9}{r^5} \right) \left(\frac{\partial}{\partial r} \right) . \tag{F-8}$$

REFERENCES

1. N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions, 2nd ed. (Oxford University Press, New York, 1949); Atomic and Molecular Processes, ed. by D. R. Bates (Academic Press, Inc., New York, 1962).
2. W. Kohn, Rev. Mod. Phys. 26, 292 (1954).
3. H. S. W. Massey, Rev. Mod. Phys. 28, 199 (1956); E. Gerjuoy, Rev. Mod. Phys. 33, 544 (1961).
4. B. Bederson, H. Malamud, and J. Hammer, Bull. Am. Phys. Soc., Ser. II, 2, 172 (1957).
5. R. T. Brackmann, W. L. Fite, and R. H. Neynaber, Phys. Rev. 112, 1157 (1958).
6. B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) 71, 877 (1958).
7. B. A. Lippmann, Bull. Am. Phys. Soc. 5, 119 (1960).
8. P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).
9. C. Schwartz, Phys. Rev. 124, 1468 (1961).

9A. M. Rotenberg, Ann. Phys. (N. Y.) 19, 262 (1962).

10. A. Temkin, Phys. Rev. 126, 130 (1962).

10A. T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

11. For a summary see H. Feshbach, Ann. Rev. Nucl. Sci. 8, 49 (1958); Proceedings of the International Conference on the Nuclear Optical Model, Tallahassee, Florida, March 1959 (Florida State University, 1959).
12. B. A. Lippmann and H. M. Schey, Phys. Rev. 121, 1112 (1961).
13. M. H. Mittleman and K. M. Watson, Phys. Rev. 113, 198 (1959); B. A. Lippmann, M. Mittleman, and K. M. Watson, Phys. Rev. 116, 920 (1959).

13A. M. H. Mittleman, Ann. Phys. (N. Y.) 14, 94 (1961).

14. R. A. Buckingham, Proc. Roy. Soc. (London) A160, 94 (1937).
15. B. A. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950).
16. V. M. Martin, M. J. Seaton, and J. B. G. Wallace, Proc. Phys. Soc. (London) 72, 701 (1958).

17. D. C. S. Allison, H. A. F. McIntyre, and B. L. Moiseiwitch, Proc. Phys. Soc. (London) 78, 1169 (1961).

18. I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. 53, 654 (1957).

19. T. L. John, Proc. Phys. Soc. (London) 76, 532 (1960).

20. K. Smith, R. P. McEachran, and P. A. Fraser, Phys. Rev. 125, 553 (1962).

21. P. G. Burke and H. M. Schey, Phys. Rev. 126, 147 (1962).

22. L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc. (London) A254, 259 (1960).

23. T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

24. A. Temkin and J. C. Lamkin, Phys. Rev. 121, 788 (1961).

25. F. B. Malik and E. Trefftz, Z. Astrophys. 50, 96 (1960).

26. R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. 121, 135 (1961).

27. R. P. McEachran and P. A. Fraser, Can. J. Phys. 38, 317 (1960); K. Smith, Phys. Rev. 120, 845 (1960); S. Geltman, Phys. Rev. 119, 1283 (1960).

28. H. B. Gilbody, R. F. Stebbing, and W. L. Fite, Phys. Rev. 121, 794 (1961).

29. P. G. Burke and H. M. Schey, Phys. Rev. 126, 163 (1962).

30. H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press, Inc., New York, 1957).

31. See footnote 23a in reference 21.

32. A. Temkin and R. Pohle, Preprint, October 1962, Theoretical Division, NASA, Goddard Space Flight Center, Greenbelt, Maryland.

33. A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) A70, 223 (1957).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.