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THE VARIATIONAL METHOD IN ELECTRON-
HYDROGEN SCATTERING

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Robert Louis Armstead
(Ph. D. Thesis)

September 3, 1964

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ABSTRACT

The Kohn variational principle is used to calculate p-wave phase shifts for the elastic scattering of electrons from a neutral hydrogen atom at subexcitation energies.

The trial wave function is represented on a basis which simplifies algebraic and numerical work.

It is found that a careful treatment avoids the usual pitfalls of variational scattering calculations and yields quite accurate results.

Singlet and triplet p-wave phase shifts are tabulated and compared with other calculations. Similar calculations for s-wave and p-wave positron-hydrogen scattering are carried out and tabulated.

I. INTRODUCTION

The scattering of charged particles from atoms has long been a fruitful technique in the study of atomic structure. Rutherford in his classic scattering experiment not only deposed the "plum pudding" atom, but forged an indispensable tool, whose usefulness has improved with sharpening. More recently the scattering of electrons and protons from atoms has provided input to calculations of kinetic processes in gases. In the case of electrons scattered from hydrogen we find applications in such fields as astrophysics¹ and thermonuclear reactions.

Naturally an understanding of the theory of atomic scattering is important, and in fact theoretical advances in the past thirty years enable us to give formal solutions to many scattering problems.² However, many calculations, even for elementary systems, remain to be done satisfactorily. Unfortunately, no experiments of sufficient accuracy to assess the various approximations so far applied to the e^-H or e^+H elastic scattering problem have yet been reported. The major reason for this deficiency is that it is difficult to convert the diatomic hydrogen molecule into monatomic hydrogen without exciting some of the atoms out of the ground state, thus making it impossible to interpret the data with confidence. Improved techniques,³ however, should soon lead to more accurate experiments.

We will consider in this paper the simplest possible atomic scattering problem: namely, that of an electron (or positron) incident

on a neutral hydrogen atom with an energy too low to induce an excitation of the atom (or formation of positronium). We will assume that the hydrogen nucleus is the center of mass of the three-body system and therefore infinitely massive compared to the electrons, that only Coulomb interactions are important, that the atom is in its ground state when the incident particle is far away before and after the interaction, that the electrons each have spin $\frac{1}{2}$, and that the requirements of the Pauli principle are satisfied. This last assumption means that when the incident particle is an electron, the wave function is antisymmetric or symmetric under exchange of the space coordinates of the two electrons according as the electron spins are aligned (triplet) or anti-aligned (singlet). This is the only way in which electron spin will enter the problem, and therefore the spin variables will never appear explicitly.

This paragon among real problems has been the subject of intensive study,⁴ and we will presently mention some of the theoretical schemes that have been applied to it. First we will consider an intuitive physical picture of the scattering process, starting with the incoming electron still far away from the target atom. Ideally the electron would not interact while yet far away because the atom is a neutral object. However, the orbital electron in the atom does feel a repulsion from the incoming electron, consequently altering its orbit and trying to hide behind the proton. This effectively brings the positive charge of the atom on the average closer than

the negative charge to the incident particle, i.e. polarizing the atom, resulting in a net attraction between the atom and the electron. Similar considerations apply when the incident particle is a positron. Various theoretical calculations⁵ have determined that this attractive force between the atom and the incident (low energy) electron has a potential of the form $-\alpha/2r^4$, where α is the polarizability, a positive constant characteristic of the atom. As the incident electron approaches and penetrates the atomic electron cloud, it creates around itself a bubble from which the cloud is excluded because of the electrons' mutual repulsion. Naturally this gives rise to some bizarre distortions of the target atom from its symmetrical ground state. At this point the incident particle cannot be treated as if it were seeing some average atomic field; the details are clearly important. When the electron leaves the atom and moves off to infinity the atom settles down, and the interaction is again controlled by the polarization effect.

From these crude intuitive considerations alone, it should be abundantly clear that solving completely even this simplest problem is a major task. If other channels are opened, that is, if the incident particle has sufficient energy to excite or ionize the atom, things get even worse. On the other hand, if we modify the problem by assuming there cannot be any distortion in the atomic wave function, then it is reduced to a single particle in a short-range central potential, and has a relatively simple solution. This is called the static

approximation and has been used somewhat,⁶ but is sufficiently different from the real situation that in most cases the results are seriously in error.

The most famous of all approximations in scattering is the first Born approximation.⁷ The Born series is just the expansion of the wave function as a power series in the strength of the scattering potential. Truncation after the nth power gives the nth Born approximation. For incident particles moving faster than the orbital electron(s) in the atom, the first Born approximation generally gives satisfactory results. However, in the region of interest to us here (less than about ten electron volts) it is usually inadequate. In this region the most popular technique is the eigenfunction expansion.⁸ That is, the complete wave function is assumed to be an infinite sum of terms, each term consisting of the product of an unperturbed atomic eigenfunction and a function (to be determined) of the position of the incident particle. (This discussion assumes for simplicity the distinguishability of the incoming particle and the atomic electron.) Solving the problem is thus relegated to determining these functions. This is done by substituting the sum into the Schroedinger equation, which results in an infinite set of coupled differential equations for the unknown functions. At this point a decision has to be made, usually on physical grounds, about which and how many of the terms in the sum to use. One advantage of this method is its direct physical interpretation because of the appearance of the atomic

eigenfunctions. Different effects (polarization, etc.) may be emphasized by judiciously selecting the terms to be kept in the expansion. However, usually no more than the first one or two (at most three)⁹ are used because of the considerable effort needed to solve the coupled equations, and it is always difficult to tell a priori how good the answers are. Furthermore, the complete sum referred to above is not only over the discrete bound states of the atom, but over the unbound (positive energy) states as well, where it is actually an integral. This region, the continuum, is always neglected in the eigenfunction expansion method. Nevertheless, this scheme in one approximation or another has been the basis for most atomic scattering calculations performed since 1932, when it was introduced by Massey and Mohr.¹⁰

Within the last fifteen years, however, a surge of activity has been directed toward the use of variational techniques in the nonrelativistic atomic scattering problem. The Rayleigh-Ritz variational principle¹¹ had established its usefulness for bound-state problems by 1940, but it was not directly applicable to scattering phenomena for two reasons: the wave functions in scattering problems are not normalizable, and the eigenvalues are in the continuous spectrum. These difficulties were overcome in 1944 by Hulthen, when he invented the variational principle bearing his name. The principle was modified to a somewhat simpler form by Kohn in 1948,¹² and it is this modification, called the Kohn variational principle, with which

the bulk of this paper will deal. A variational principle was developed by Schwinger in 1947,¹³ derived from an integral form of the Schroedinger equation. (Hulthen and Kohn began with the ordinary differential Schroedinger equation.) It involves integral expressions which are difficult to evaluate, however, and has not been as useful as the simpler equations of Kohn and Hulthen.

In part II after a brief sketch of the standard partial wave expansion to establish notation, we shall derive the Kohn principle for partial wave phase shifts and discuss a trial function appropriate to elastic e^+H and e^-H scattering. The singularities noticed and explained by Schwartz¹⁴ will be reviewed, as well as his effective cure for them. Results of our calculations for the e^-H p wave and the e^+H s and p wave phase shifts are given in part III along with a discussion and comparison with results of other workers' calculations.

II. THE VARIATIONAL METHOD

Our first task in this section will be to review briefly the standard (Faxen-Holtzmark)¹¹ expansion of the scattering wave function into partial waves of definite angular momentum. In part B we will derive the Kohn variational principle for the simple case of scattering by a fixed short-range potential. This will provide us with the essentials to solve the elastic electron-hydrogen or positron-hydrogen scattering problem. In part C we will describe in some detail the actual procedure for calculating the p-wave phase shift, an interesting difficulty encountered, and a resolution of that difficulty. Throughout the paper we will use units such that \hbar (Planck's constant), m (mass of the electron), and e (charge on the electron) each have unit magnitude.

A. Partial Waves

Suppose a flux of particles of momentum \vec{k} is incident upon a spherically symmetric potential, $V(r)$, that vanishes outside a finite region of space. Taking the center of the scattering region as the coordinate origin, the total wave function at large r is the sum of the incident wave $e^{i\vec{k}\cdot\vec{r}}$ and the scattered wave $\frac{e^{ikr}}{r} f(\theta)$, where $f(\theta)$ describes the angular distribution and is called the "scattering amplitude." Therefore,

$$\psi(\vec{r}) \xrightarrow{r \rightarrow \infty} e^{i\vec{k}\cdot\vec{r}} + f(\theta) \frac{e^{ikr}}{r}$$

is the asymptotic solution to the Schroedinger equation

$$\left[-\frac{\nabla^2}{2} - \frac{k^2}{2} + v(r) \right] \psi(\vec{r}) = 0 .$$

The angle θ is measured from the direction of \vec{k} . If we define the differential cross section $\sigma(\theta)$ as the ratio of the number of particles scattered per unit time into unit solid angle at θ to the incident flux of particles, then $\sigma(\theta) = |f(\theta)|^2$. This follows easily from the definition:

$$\sigma(\theta)d\Omega = \frac{\left| \frac{e^{ikr}}{r} f(\theta) \right|^2 kr^2 d\Omega}{\left| e^{i\vec{k}\cdot\vec{r}} \right|^2 k} = |f(\theta)|^2 d\Omega .$$

The differential cross section may be measured experimentally, and the quantity $|f(\theta)|^2$ is therefore the link between experiment and theory. Another way to approach the problem is to expand the complete wave function in partial waves of definite angular momentum l ,

$$\psi(\vec{r}) = \sum_{l=0}^{\infty} \psi_l(\vec{r}) ,$$

where

$$\psi_l(\vec{r}) = \frac{\phi_l(r)}{r} Y_{l0}(\theta) .$$

$Y_{l0}(\theta)$ is a spherical harmonic of order l and magnetic quantum number zero, and will henceforth be written simply $Y_l(\theta)$. The azimuthal angle ϕ does not appear because of cylindrical symmetry about \vec{k} . Then $\phi_l(r)$ satisfies the radial Schroedinger equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{k^2}{2} + \frac{l(l+1)}{2r^2} + V(r) \right] \phi_l(r) = 0. \quad (1)$$

There are two independent, real solutions of Eq. (1) if $V = 0$. They are $rj_l(kr)$ and $rn_l(kr)$, where j_l and n_l are called, respectively, the spherical Bessel and spherical Neumann functions of order l . They have the following properties for small and large r :

$$j_l(kr) \xrightarrow{r \rightarrow 0} \frac{(kr)^l}{(2l+1)!!},$$

$$j_l(kr) \xrightarrow{r \rightarrow \infty} \frac{\sin(kr - \frac{l\pi}{2})}{kr} + \frac{l(l+1)}{2} \frac{\cos(kr - \frac{l\pi}{2})}{(kr)^2},$$

$$n_l(kr) \xrightarrow{r \rightarrow 0} -\frac{(2l-1)!!}{(kr)^{l+1}},$$

$$n_l(kr) \xrightarrow{r \rightarrow \infty} -\frac{\cos(kr - \frac{l\pi}{2})}{kr} + \frac{l(l+1)}{2} \frac{\sin(kr - \frac{l\pi}{2})}{(kr)^2}.$$

If there is no scattering (i.e. $V = 0$ everywhere), clearly $rj_l(kr)$ is the only physically acceptable solution of (1) since $n_l(kr)$ blows up at the origin. However, if V is nonzero in some region then outside this region the solution of (1) must be a linear combination of the form

$$\phi_l(r) = A_l r j_l(kr) - B_l r n_l(kr),$$

where B_ℓ need not be zero. The k -dependent ratio B_ℓ/A_ℓ obviously characterizes the scattering of the ℓ th partial wave, and the phase shift η_ℓ is then defined as $\tan \eta_\ell = B_\ell/k_\ell$. The complete solution of Eq. (1) has boundary conditions

$$\phi_\ell(r) \xrightarrow{r \rightarrow \infty} \frac{\sin(kr - \frac{\ell\pi}{2})}{k} + \tan \eta_\ell \frac{\cos(kr - \frac{\ell\pi}{2})}{k} = \frac{\sin(kr - \frac{\ell\pi}{2} + \eta_\ell)}{k \cos \eta_\ell}$$

and

$$\phi_\ell(r) \underset{r \rightarrow 0}{\sim} r^{\ell+1}.$$

The former follows from the asymptotic forms of j_ℓ and η_ℓ , and the latter follows directly from (1) considered for r sufficiently small that k^2 and V are negligible compared to the centrifugal term $\frac{\ell(\ell+1)}{2r^2}$.

If we also expand $f(\theta)$ in terms of spherical harmonics, we may determine the coefficients in terms of the phase shifts η_ℓ .

This just takes a few lines of algebra and yields

$$f(\theta) = \sum_{\ell=0}^{\infty} \frac{\sqrt{4\pi} \sqrt{2\ell+1}}{2ik} \left[e^{2i\eta_\ell} - 1 \right] Y_\ell(\theta).$$

The total cross section $Q = \int \sigma(\theta) d\Omega = \int |f(\theta)|^2 d\Omega = \sum_{\ell=0}^{\infty} Q_\ell$, where

$$Q_\ell = \frac{4\pi}{k^2} (2\ell+1) \sin^2 \eta_\ell.$$

We have made use of the orthonormality of the $Y_\ell(\theta)$ in the angular integration. The solution to the scattering problem is thus

reduced to determining all the phase shifts η_ℓ . Fortunately in the low energy region the phase shifts for large ℓ are usually small enough to neglect when computing the cross section.

B. Kohn Variational Principle¹²

We will now investigate a variational method for calculating the phase shifts η_ℓ . The purpose of any variational scheme is to provide a functional of the wave function which is exactly equal to the desired quantity (in our case the phase shift) when the wave function is exactly correct, and which is in error only by terms of second order in the wave function error when the wave function is not exactly correct. Roughly speaking, this means that a 10% error in the wave function will give only a 1% error in the phase shift.

Consider the functional

$$F(\psi) = \int \psi(\vec{r})(H - E)\psi(\vec{r})d\vec{r}$$

where the integration is taken over all space. If ψ is allowed to vary, i.e. $\psi(\vec{r}) \rightarrow \psi(\vec{r}) + \delta\psi(\vec{r})$, then

$$\delta F = \int \delta\psi(H - E)\psi d\vec{r} + \int \psi(H - E)\delta\psi d\vec{r} + \int \delta\psi(H - E)\delta\psi d\vec{r} \quad (2)$$

is the corresponding variation in F . For our single particle in a central field $V(r)$, $H = -\frac{\nabla^2}{2} + V(r)$, and a partial integration of the second term on the right-hand side of (2) yields

$$\delta F = 2 \int \delta\psi(H - E)\psi d\vec{r} + \frac{1}{2} \int \nabla \cdot [\delta\psi \nabla \psi - \psi \nabla \delta\psi] d\vec{r} + \int \delta\psi(H - E)\delta\psi d\vec{r},$$

since

$$\nabla^2 \delta\psi = \nabla \cdot (\psi \nabla \delta\psi) - \nabla \cdot (\delta\psi \nabla \psi) + \delta\psi \nabla^2 \psi.$$

The second integral on the right-hand side may be converted to a surface integral over a sphere of very large radius R ; thus

$$\delta F = 2 \int \delta\psi (H - E)\psi \, d\vec{r} + \frac{1}{2} \int_{R \rightarrow \infty} \left[\delta\psi \frac{\partial}{\partial r} \psi - \psi \frac{\partial}{\partial r} \delta\psi \right] dS + \int \delta\psi (H - E)\delta\psi \, d\vec{r}. \quad (3)$$

So far no conditions have been imposed on the function $\psi(\vec{r})$. If we now constrain ψ and $\delta\psi$ to fall off faster than $1/r$ at large r , then the surface integral vanishes as $R \rightarrow \infty$, and we obtain the Rayleigh-Ritz principle for bound states. We have

$$\delta F = 2 \int \delta\psi (H - E)\psi \, d\vec{r} + \int \delta\psi (H - E)\delta\psi \, d\vec{r}.$$

Or, rewriting it,

$$F(\psi_t) - F(\psi) = 2 \int (\psi_t - \psi)(H - E)\psi \, d\vec{r} + \int (\psi_t - \psi)(H - E)(\psi_t - \psi) \, d\vec{r}, \quad (4)$$

where ψ_t is the trial function, which need not satisfy the Schroedinger equation $(H - E)\psi = 0$, and ψ is the correct solution. Then the first integral on the right-hand side of (4) is zero, and the difference

$$F(\psi_t) - F(\psi) = \int (\psi_t - \psi)(H - E)(\psi_t - \psi) \, d\vec{r} \quad (5)$$

is second order in the error $\psi_t - \psi$. Ordinarily, the energy E is the quantity to be calculated in bound-state problems. If ψ and ψ_t are each normalized to unity, then if we define $\langle E \rangle = \int \psi_t H \psi_t d\vec{r}$,

$$\int \psi_t H \psi_t d\vec{r} - \int \psi H \psi d\vec{r} = F(\psi_t) - F(\psi) = \langle E \rangle - E$$

from the definition of F ; therefore from (5),

$$\langle E \rangle = E + \int (\psi_t - \psi)(H - E)(\psi_t - \psi) d\vec{r}.$$

This means that $\langle E \rangle$ is correct to first order; furthermore if E is the lowest energy eigenvalue, the second order error term is always positive, as may easily be seen directly by expanding the function $\psi_t - \psi$ in eigenfunctions of the operator H . One procedure, then, is to guess a function ψ_t , calculate the quantity $\langle E \rangle = \int \psi_t H \psi_t$ and rest assured that it is an upper bound on the correct energy eigenvalue E . Typically, however, we would expand ψ_t in a convenient set of functions $\psi_t = \sum_{i=0}^{\infty} C_i u_i$, determine the parameters C_i by $\partial F_t / \partial C_i = 0$, and solve the resulting characteristic equation $\det |H_{ij} - \langle E \rangle M_{ij}| = 0$ for $\langle E \rangle$, where

$$H_{ij} = \int u_i H u_j d\vec{r}$$

and

$$M_{ij} = \int u_i u_j d\vec{r}.$$

It is shown by MacDonald¹⁵ that as N is increased, the lowest eigenvalues of H are approached monotonically by the solutions $\langle E \rangle$, so

that we can always get a better answer by doing more work. This state of affairs could hardly be more satisfactory, so we now drop it and return to the more interesting scattering question. Now the remarks following Eq. (3) do not apply, since scattering wave functions are not normalizable, and the energy is given, not calculated. The quantity to be calculated is the phase shift η_l . We now restrict ψ so that

$$\begin{aligned} \psi \xrightarrow{r \rightarrow \infty} & \left[\frac{\sin(kr - \frac{l\pi}{2})}{kr} + \tan \eta \frac{\cos(kr - \frac{l\pi}{2})}{kr} \right] Y_l(\theta) \\ & = \frac{\sin(kr - \frac{l\pi}{2} + \eta)}{\cos \eta kr} Y_l(\theta), \end{aligned}$$

$$\delta\psi \xrightarrow{r \rightarrow \infty} \delta(\tan \eta) \frac{\cos(kr - \frac{l\pi}{2})}{kr} Y_l(\theta),$$

and

$$\delta\psi, \quad \psi \xrightarrow{r \rightarrow 0} 0,$$

where the l subscript is henceforth understood on ψ and η .

Thus ψ must have the correct asymptotic form, except that η may be varied. Now Eq. (3) yields

$$\begin{aligned} \delta F &= 2 \int \delta\psi(H-E)\psi \, d\vec{r} + \frac{1}{2} \delta(\tan \eta) \int_{R \rightarrow \infty} \left[\frac{\cos(kR - \frac{l\pi}{2})\cos(kR - \frac{l\pi}{2} + \eta)}{k R^2 \cos \eta} \right. \\ & \quad \left. + \frac{\sin(kR - \frac{l\pi}{2} + \eta)\sin(kR - \frac{l\pi}{2})}{k R^2 \cos \eta} + O\left(\frac{1}{R^3}\right) \right] Y_l^2(\theta) R^2 d\Omega + \int \delta\psi(H-E)\delta\psi \, d\vec{r}, \\ &= 2 \int \delta\psi(H-E)\psi \, d\vec{r} + \frac{\delta(\tan \eta)}{2k} + \int \delta\psi(H-E)\delta\psi \, d\vec{r}, \end{aligned}$$

or

$$\delta\left(F - \frac{\tan \eta}{2k}\right) = 2 \int \delta\psi(H - E)\psi \, d\vec{r} + \int \delta\psi(H - E)\delta\psi \, d\vec{r} . \quad (6)$$

Equation (6) is the basis for the Kohn and Hulthen variational principles. Defining $I = \frac{\tan \eta}{k} - 2F$, we notice three things about the equation:

1. If ψ is the correct scattering solution of $(H - E)\psi = 0$, then $\delta I = 0$ to first order, and $I = \tan \eta/k$ where η is correct, since $F = 0$.

2. If I is stationary (i.e. $\delta I = 0$ to first order) for arbitrary excursions $\delta\psi$ from ψ , then ψ is the correct solution of $(H - E)\psi = 0$, since the first term on the right-hand side of (6) must then be zero. $(H - E)\psi = 0$ follows by letting $\delta\psi = \epsilon(H - E)\psi$, ϵ a small number.

3. If some incorrect ψ , call it ψ_t , is used to calculate I_t (the error in the wave function being $\delta\psi = \psi_t - \psi$), then I_t differs from $I (= \frac{\tan \eta}{k})$ by $O(\delta\psi)^2$. To see this, notice that ψ in Eq. (6) is replaced by ψ_t , that $\psi_t = \psi + \delta\psi$, and that $(H - E)\psi = 0$.

Conclusions 1 and 2 say that $\delta I = 0$ and $(H - E)\psi = 0$ are completely equivalent; conclusion 3 is an important feature in calculations.

Analogous to the Ritz procedure, we equate ψ_t to its asymptotic form plus a sum of functions chosen to approximate the correct solution for small r .

$$\psi_t = Y_\ell(\theta) \left[j_\ell(kr) - \tan \eta_t n_\ell(kr) g(r) \right] + \sum_{i=1}^N C_i u_i(r),$$

where $u_i(r)$ are the "close-in" basis functions. The function $g(r)$ is just a device put in to squash the singularity of n_ℓ at the origin and go to unity at large r , and is of no interest to us now (in fact will be found later to be unnecessary because of a slightly different asymptotic form). There are $N+1$ parameters to be chosen: namely C_i for $i = 1, 2, \dots, N$, and $\tan \eta_t/k$.

Before continuing, we point out that it is not possible to determine the sign of the (second order) error as we did for the bound state problem except in the case that $E = 0$. (The zero energy case is important for s-wave scattering and has been extensively studied; however it will not concern us here.) Therefore, we never know whether we have an upper or lower bound on the phase shift, and in fact we may have neither.¹⁶ Consequently it is no longer clear that the correct way to choose the C_i 's and $\tan \eta_t$ is to set the first derivative of I with respect to $\tan \eta_t$ and each of the C_i equal to zero. Nevertheless, this is what Kohn prescribes, and we believe that it is a reasonable prescription to follow, particularly since we find respectable convergence in an actual calculation as N is increased. A simple example may dispel some doubt about the scheme.

Suppose that through some preposterous stroke of luck we were to choose as the trial function for the s wave

$$\psi_t = \left[\psi - g \tan \eta \frac{\cos kr}{\sqrt{4\pi} kr} \right] + g \tan \eta_t \frac{\cos kr}{\sqrt{4\pi} kr} .$$

That is, the correct wave function except for an undetermined phase shift. Does our recipe yield the correct phase and hence the correct wave function?

$$I_t = -2 \int \left[\psi - g \Delta \frac{\cos kr}{\sqrt{4\pi} kr} \right] (H - E) \left[\psi - g \Delta \frac{\cos kr}{\sqrt{4\pi} kr} \right] d\vec{r} + \frac{\tan \eta_t}{k} ,$$

where

$$\Delta = \tan \eta - \tan \eta_t .$$

$$I_t = +2 \Delta \int \left[\sqrt{4\pi} \psi - g \Delta \frac{\cos kr}{kr} \right] (H - E) g \frac{\cos kr}{kr} \frac{d\vec{r}}{4\pi} + \frac{\tan \eta_t}{k}$$

$$= \Delta \int_{R \rightarrow \infty} \left[\frac{\cos kR}{kR} \frac{\partial}{\partial R} \frac{\sin(kR + \eta)}{\cos \eta kR} - \frac{\sin(kR + \eta)}{\cos \eta kR} \frac{\partial}{\partial R} \frac{\cos kR}{kR} \right] \frac{dS}{4\pi} - 2\Delta^2 C + \frac{\tan \eta_t}{k} ,$$

where a partial integration has been used along with $(H - E)\psi = 0$, and the integral involving g^2 is just some number C .

$$I_t = + \frac{\Delta}{k} \frac{\cos \eta}{\cos \eta} - 2\Delta^2 C + \frac{\tan \eta_t}{k} ,$$

and

$$\frac{\partial I_t}{\partial \tan \eta_t} = 0 \quad \text{gives} \quad - \frac{1}{k} + 4C(\tan \eta - \tan \eta_t) + \frac{1}{k} = 0 .$$

Therefore $\tan \eta_t = \tan \eta = \tan \eta$.

Using the exact solution,

Therefore

$$\tan \eta_t = \tan \eta = I_t k ,$$

giving us the exact solution.

In summary, the Kohn principle specifies that we calculate

$$I_t = \frac{\tan \eta_t}{k} - 2 \int \psi_t (H - E) \psi_t d\vec{r} ,$$

where ψ_t contains N constants C_i as well as the phase η_t , and

$$\psi_t \xrightarrow{r \rightarrow \infty} \frac{\sin(kr - \frac{\ell\pi}{2} + \eta_t)}{\cos \eta_t kr} Y_\ell(\theta) ,$$

where the C_i and $\tan \eta_t$ are determined by

$$\frac{\partial I_t}{\partial C_i} = 0 \quad \text{and} \quad \frac{\partial I_t}{\partial \tan \eta_t} = 0 . \quad (7)$$

Then I_t is expected to be very close to the correct $\tan \eta/k$.

The Hulthen principle is identical except that the C_i and $\tan \eta_t$ are determined by

$$\frac{\partial I_t}{\partial C_i} = 0 \quad \text{and} \quad I_t = 0 . \quad (8)$$

It is harder to use because the second condition of (8) is quadratic in $\tan \eta_t$, whereas (7) is linear.

Notice also that the Hulthen principle gives the wrong answer in our example. $I_t = 0$ yields

$$\tan \eta_t = \tan \eta - \sqrt{\frac{\tan \eta}{2k C}} .$$

Of course this is not proof that Kohn's principle is always more accurate. Some counterexamples are given in the article by Makinson and Turner.¹⁶ We will do all our calculations with the Kohn principle because it is simpler to use, and because there is no a priori reason to prefer the other.

{ note: see Malik, Annals of Physics 20, 464-478 (1962) (Malik shows an equivalence between Kohn's & Hulthén's) }

C. Singularities

It has been known for some time¹⁴ that a straightforward application of a variational principle to scattering problems often yields unsatisfactory results. A detailed study of this "inadequacy" was made by Schwartz,¹⁴ and we now review his arguments.

We start by examining the variational scheme closely, still restricting ourselves to potential scattering. The trial function for the l th partial wave is

$$\psi_t(\vec{r}) = \phi_0(\vec{r}) + \lambda_t \phi_1(\vec{r}) + \sum_{i=1}^N c_i u_i(\vec{r}) ,$$

where

$$\phi_0(\vec{r}) \xrightarrow{r \rightarrow \infty} \frac{\sin(kr - \frac{l\pi}{2})}{kr} Y_l(\theta) ,$$

$$\phi_1(\vec{r}) \xrightarrow{r \rightarrow \infty} \frac{\cos(kr - \frac{l\pi}{2})}{r} Y_l(\theta) ,$$

$$\lambda_t = \frac{\tan \eta_t}{k} ,$$

and where the $u_i(r)$ go to zero for large r and approach zero (as do ϕ_0

and ϕ_1) as $r \rightarrow 0$ at least as fast as r^l . All quantities are taken to be real. The variational principle is

$$[\lambda] = I_t = \lambda_t - 2 \int \psi_t (H - E) \psi_t d\vec{r},$$

where $[\lambda]$ is $\tan \eta/k$ correct to first order. Substitution of ψ_t into the integral yields

$$[\lambda] = B_0 + \lambda_t B_1 + \lambda_t^2 B_2 + 2 \sum_{i=1}^N c_i R_{0i} + 2\lambda_t \sum_{i=1}^N c_i R_{1i} + \sum_{i,j=1}^N c_i c_j M_{ij} + \lambda_t, \quad (9)$$

where

$$B_0 = -2 \int \phi_0 (H - E) \phi_0 d\vec{r},$$

$$B_1 = -2 \int \phi_0 (H - E) \phi_1 d\vec{r} - 2 \int \phi_1 (H - E) \phi_0 d\vec{r},$$

$$B_2 = -2 \int \phi_1 (H - E) \phi_1 d\vec{r},$$

$$R_{0i} = -2 \int \phi_0 (H - E) u_i d\vec{r},$$

$$R_{1i} = -2 \int \phi_1 (H - E) u_i d\vec{r},$$

and

$$M_{ij} = -2 \int u_i (H - E) u_j d\vec{r}.$$

As usual, the integrations extend over all space. Since the functions u_i vanish exponentially for large r , it is clear that $H-E$ is

Hermitean with respect to them, and thus $M_{ij} = M_{ji}$. In vector notation (9) becomes

$$[\lambda] = B_0 + \lambda_t B_1 + \lambda_t^2 B_2 + 2 \vec{c} \cdot \vec{R}_0 + 2 \lambda_t \vec{c} \cdot \vec{R}_1 + \vec{c} \cdot M \cdot \vec{c} + \lambda_t \quad (11)$$

setting

$$\frac{\partial[\lambda]}{\partial c_1} = 0$$

yields

$$-M \cdot C = R_0 + \lambda_t R_1.$$

Therefore, set $C = C_0 + \lambda_t C_1$, so that

$$R_0 = -M C_0$$

$$R_1 = -M C_1.$$

(12)

Then (11) becomes

$$[\lambda] = B_0 + C_0 \cdot R_0 + \lambda_t [B_1 + C_1 \cdot R_0 + C_0 \cdot R_1 + 1] + \lambda_t^2 [B_2 + C_1 \cdot R_1].$$

Making $[\lambda]$ stationary with respect to λ_t then gives

$$\lambda_t = \frac{-[B_1 + C_1 \cdot R_0 + C_0 \cdot R_1 + 1]}{2[B_2 + C_1 \cdot R_1]},$$

and finally

$$[\lambda] = B_0 + C_0 \cdot R_0 - \frac{[B_1 + C_1 \cdot R_0 + C_0 \cdot R_1 + 1]^2}{4[B_2 + C_1 \cdot R_1]}, \quad (13)$$

which we hope is close to the correct $\lambda = \tan \eta/k$, since it differs only by second order in the wave function error.

The Hamiltonian H is an operator that has a continuous spectrum (the scattering states) as well as (possibly) a discrete spectrum of eigenvalues (the bound states). The continuous spectrum contains the eigenvalue E ; hence the spectrum of the operator $H - E$ includes zero. In this scheme $H - E$ is represented on a basis of N functions u_i , and as N goes to infinity we expect the matrix M to become a complete representation of $H - E$. We therefore also expect that as N grows (but remains finite) we may occasionally run across an eigenvalue of M that is very close to zero. While it is not likely we will hit a zero eigenvalue exactly, it is likely that the number of eigenvalues within any neighborhood of zero will increase as N increases. This means that the matrix M may become nearly singular, and therein lie the vagaries of the variational method. The effect on $[\lambda]$ may be traced from the solution of Eqs. (12). Suppose M has eigenvectors $\vec{\xi}_m$ corresponding to eigenvalues ϵ_m , i.e. $M \vec{\xi}_m = \epsilon_m \vec{\xi}_m$, $m = 1, \dots, N$. Then the solution to (12) is

$$\vec{c} = - \sum_{m=1}^N \frac{(\vec{R} \cdot \vec{\xi}_m)}{\epsilon_m} \vec{\xi}_m,$$

and

$$\vec{R} \cdot \vec{c} = - \sum_{m=1}^N \frac{(\vec{R} \cdot \vec{\xi}_m)^2}{\epsilon_m}. \quad (14)$$

Terms of this form occur in the stationary expression for $[\lambda]$, Eq. (12). If some ϵ_m becomes very small, the magnitude of the corresponding term in (13), and therefore of $[\lambda]$, may become huge, and the resulting error in $[\lambda]$ very large. We still need to examine the numerator of the right-hand side of (14) to see if $\vec{R} \cdot \vec{\xi}_m$ is automatically small when ϵ_m is small, thus eliminating singularities of this kind. Suppose $\epsilon_m = 0$. Then $\sum_{k=1}^N M_{ik}(\vec{\xi}_m)_k = 0$, $i = 1, \dots, N$. That is,

$$\sum_{k=1}^N \int u_1(H - E)u_k(\vec{\xi}_m)_k = 0.$$

This says that the function $(H - E) \sum_{k=1}^N u_k(\vec{\xi}_m)_k$ is orthogonal to each of the functions u_k ; however we have no reason to expect it to be orthogonal to ϕ_0 or ϕ_1 , since they are unrelated to the u_i 's. Therefore the numerator need not be zero. If we were using a complete set of u_i 's, then $\vec{R} \cdot \vec{\xi}_m$ would have to be zero, since we could imagine the ϕ 's expanded in terms of the u_i . With a finite set of u_i , however, we are always in danger of a possible infinity. Nevertheless, as N grows and the basis becomes more complete, we hope for weaker singularities (i.e. smaller $R \cdot \xi_m$) and reasonable convergence.

This plight is analogous to seeking the stationary value of the quadratic expression

$$y = ax^2 + bx + c$$

when a becomes small. For nonzero a , it is

$$y_s = \frac{-b^2}{4a} + c.$$

If $a = 0$, a stationary value exists only if b is also zero, and if a approaches zero the magnitude of y_s becomes arbitrarily large. In this analogy, a corresponds to M , x corresponds to \vec{C} , and b corresponds to \vec{R} .

The upshot of this analysis is that by working harder we may at any step only succeed in climbing a pole and getting a worse answer than we already had. We solve this problem by parameterizing the subspace of functions $u_i(r)$ by a single parameter α (not the polarizability). Varying α allows us to vary the subspace in a continuous fashion and thus map out the behavior of $[\lambda]$, exposing the singularities as well as regions of good behavior. We look for convergence with increasing N in these "good" regions. This method was devised and tested by Schwartz¹⁷ in calculations for e^-H and e^+H , s-wave, elastic scattering, and worked beautifully. (As an example, we might use $u_i(r) = r^{i-1}(e^{-\alpha r})$ in an s-wave calculation for our one-body, potential scattering.) Our own calculations of p-wave scattering display similar qualitative features and appear to yield good results, as we will see later. In practice we fix α , calculate $[\lambda]$ for several values of N , then increment α and repeat. We find that a plot of $[\lambda]$ vs. α for a given energy gives a set of curves corresponding to the set of values N , smooth except

for the (expected) singularities, containing stationary regions, and becoming flatter and more closely spaced as N is increased. Examples for specific calculations will be given later.

D. Electron-Hydrogen Scattering

We turn now to the problem of interest: we replace the scattering potential by a hydrogen atom. This introduces three complications:

1. There are now three additional degrees of freedom.
2. The Pauli principle must be observed if the incident particle is an electron.
3. The potential is no longer short range; its leading term (in the adiabatic approximation) goes as $1/r^4$ for large r because of the polarization effect.

In reply,

1. We select as coordinates $r_1, \theta_1, r_2, \theta_2,$ and r_{12} , where the coordinate origin is taken to be the hydrogen nucleus, and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. The angles θ_1 and θ_2 are measured from the initial direction of motion of the incident electron.
2. The trial function for e^-H is constructed to be anti-symmetric or symmetric under the interchange $\vec{r}_1 \leftrightarrow \vec{r}_2$ for triplet or singlet states.
3. The wave function is no longer simply a linear combination of j_l and n_l at large r . This question will be examined in detail in the next section.

The complete Hamiltonian becomes

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} \pm \frac{1}{r_{12}} \mp \frac{1}{r_1} - \frac{1}{r_2},$$

where upper signs correspond to e^-H , lower to e^+H . We next look at the trial function.

1. Asymptotic Wave Function

We seek the appropriate asymptotic form for the trial function using a method suggested by Schwartz.¹⁸ For the moment assume that the incident and atomic electrons are distinguishable, so that we can neglect the Pauli principle. Let \vec{r}_1 be the coordinate of the incident and \vec{r}_2 the coordinate of the atomic electron. In the lowest approximation there will be no interaction at large separation between the incident particle and the atom in its ground state. This amounts to simply neglecting the interaction term $\frac{1}{r_{12}} - \frac{1}{r_1}$ for large r_1 . If $\phi(r_2)$ represents the unperturbed atomic wave function, the two-body wave function ψ_0 will then be

$$\psi_0(\vec{r}_1, \vec{r}_2) = \phi(r_2) \left[j_\ell(kr_1) - \tan \eta_\ell n_\ell(kr_1) \right] Y_\ell(\theta_1)$$

at large r_1 . As $r_1 \rightarrow \infty$, this approaches

$$\phi(r_2) \frac{\sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell)}{\cos \eta_\ell} Y_\ell(\theta_1).$$

Now expand the wave function for large r_1 as

$$(k \cos \eta_\ell) r_1 \psi(r_1, r_2) = \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1) + \frac{W(\vec{r}_1, \vec{r}_2)}{r_1} + \frac{X(\vec{r}_1, \vec{r}_2)}{r_1^2} + \dots, \quad (15)$$

where the functions W and X satisfy

$$\frac{\partial^2}{\partial r_1^2} W = -k^2 W \quad \text{and} \quad \frac{\partial^2}{\partial r_1^2} X = -k^2 X,$$

but are otherwise undetermined. Let H_0 and E_0 be the Hamiltonian and energy for the ground state atomic wave function so that

$$(H_0 - E_0) \phi(r_2) = 0.$$

Then the Schroedinger equation for $r_1 \psi$ is

$$\left[(H_0 - E_0) - \frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{k^2}{2} + \frac{L_1^2}{2r_1^2} - \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \right] r_1 \psi = 0, \quad (16)$$

where L_1^2 is the angular momentum operator. Substituting the expansion (15) into (16) and keeping terms through $O(1/r_1^2)$ yields

$$\begin{aligned} & \frac{1}{r_1} (H_0 - E_0) W + \frac{1}{r_1^2} (H_0 - E_0) X + \frac{\ell(\ell+1)}{2r_1^2} \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1) + \frac{1}{r_1} \frac{\partial W}{\partial r_1} \\ & = -\frac{r_2}{r_1} \hat{r}_1 \cdot \hat{r}_2 \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1), \end{aligned}$$

where use has been made of $\frac{1}{r_{12}} = \frac{1}{r_1} + \frac{r_2}{r_1^2} \hat{r}_1 \cdot \hat{r}_2 + \dots$

Equating coefficients of $1/r_1$ gives $(H_0 - E_0)W = 0$. This implies that

$$W(\vec{r}_1, \vec{r}_2) = \phi(r_2) Y_\ell(\theta_1) \omega(r_1).$$

Equating coefficients of $1/r_1^2$ gives

$$\begin{aligned} (H_0 - E_0)X + \frac{\ell(\ell+1)}{2} \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1) + \phi Y_\ell(\theta_1) \frac{d\omega}{dr_1} \\ = -r_2 \hat{r}_1 \cdot \hat{r}_2 \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1). \end{aligned}$$

Multiplying this by $\phi(r_2)$ and integrating over \vec{r}_2 yields

$$\frac{\ell(\ell+1)}{2} \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) + \frac{d\omega}{dr_1} = 0,$$

since

$$\int \phi(H_0 - E_0)X d\vec{r}_2 = \int X(H_0 - E_0)\phi d\vec{r}_2 = 0$$

and

$$\int r_2 \phi \hat{r}_2 \phi d\vec{r}_2 = 0.$$

Therefore

$$\omega(r_1) = \frac{\ell(\ell+1)}{2k} \cos(kr_1 - \frac{\ell\pi}{2} + \eta_\ell),$$

and we have obtained the asymptotic wave function correct to $O(1/r_1^2)$.

In fact, we see that turning on the interaction $\frac{1}{r_{12}} - \frac{1}{r_1}$ for large r_1 (allowing the atom to polarize) has not changed the form of the far-out wave function through order $1/r_1^2$ (i.e., it is the same as

$j_\ell - \tan \eta_\ell n_\ell$ through $O(1/r_1^2)$). In order to find the $1/r_1^3$ term, however, we would have to solve the remaining equation

$$(H_0 - E_0)X = -r_2 \hat{r}_1 \cdot \hat{r}_2 \phi \sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell) Y_\ell(\theta_1),$$

which clearly does involve the polarization. We will instead be content to take for the asymptotic part of ψ something that goes for large r_1 as

$$\begin{aligned} \phi(r_2) & \left[\frac{\sin(kr_1 - \frac{\ell\pi}{2} + \eta_\ell)}{kr_1 \cos \eta_\ell} + \frac{\ell(\ell+1)}{2(kr_1)^2} \frac{\cos(kr_1 - \frac{\ell\pi}{2} + \eta_\ell)}{\cos \eta_\ell} \right] Y_\ell(\theta_1) \\ & = Y_\ell(\theta_1) \phi(r_2) \left\{ \frac{\sin(kr_1 - \frac{\ell\pi}{2})}{kr_1} + \frac{\ell(\ell+1)}{2(kr_1)^2} \cos(kr_1 - \frac{\ell\pi}{2}) \right. \\ & \quad \left. + \tan \eta_\ell \left[\frac{\cos(kr_1 - \frac{\ell\pi}{2})}{kr_1} - \frac{\ell(\ell+1)}{2(kr_1)^2} \sin(kr_1 - \frac{\ell\pi}{2}) \right] \right\}, \end{aligned} \quad (17)$$

and let the (variationally determined) close-in functions take care of the polarization.

In practice we could use

$$\psi = \left[j_\ell(kr_1) - \tan \eta_\ell n_\ell(kr_1) g_\ell(r_1) \right] \phi(r_2) Y_\ell(\theta_1) + \text{close-in functions}$$

for a trial function, where g_ℓ is constructed to shield the singularity of n_ℓ at the origin; but the integrals then become difficult to evaluate numerically for $\ell \geq 1$ because of the $n_\ell g_\ell$ term. We

have invented the following more convenient function:

$$\psi = \left\{ j_\ell(kr_1) - \tan \eta_t \left[j_{\ell+1}(kr_1) + \frac{\ell+1}{kr_1} j_{\ell+2}(kr_1) \right] \right\} Y_\ell(\theta_1) \phi(r_2)$$

+ close-in functions,

which enables us to do the integrations with relative ease, yet has the required asymptotic form (17). Of course $\phi(r_2) = 2e^{-r_2}/\sqrt{4\pi}$, the normalized hydrogen ground state wave function. For e^-H scattering, ψ is operated upon by $(1 \pm P_{12})/\sqrt{2}$, where P_{12} exchanges coordinates \vec{r}_1 and \vec{r}_2 , so that

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{-2(1 \pm P_{12})}{\sqrt{4\pi} \sqrt{2}} \left\{ j_\ell(kr_1) - \tan \eta_t \left[j_{\ell+1}(kr_1) + \frac{\ell+1}{kr_1} j_{\ell+2}(kr_1) \right] \right\}$$

$\times Y_\ell(\theta_1) e^{-r_2} + \text{close-in functions.}$

The upper/lower sign is used for the single/triplet case.

2. Close-in Functions

The close-in functions (the u_i of section IIB) should:

1. be a complete basis when $N \rightarrow \infty$,
2. vanish for large r_1 or r_2 ,
3. be able to describe the electron correlations,
4. contain the non-linear parameter α ,
5. have the correct properties under a rotation; that is, a p-state must rotate like a vector, etc.,

6. be explicitly symmetric or antisymmetric under $\vec{r}_1 \leftrightarrow \vec{r}_2$ for e^-H scattering.

In his s-wave calculations, Schwartz used the function

$$\sum_{j+m+n \leq N} \exp\left[-\frac{\alpha}{2}(r_1 + r_2)\right] r_{12}^j \frac{(r_1^m r_2^n + r_1^n r_2^m)}{\sqrt{2}} C_{jmn}.$$

For our p-wave calculation we use

$$\sum_{j+m+n \leq N} \exp\left[-\frac{\alpha}{2}(r_1 + r_2)\right] r_{12}^j \frac{r_1^m r_2^n \vec{r}_1 + r_1^n r_2^m \vec{r}_2}{\sqrt{2}} C_{jmn}.$$

Calculations are done for $N = 1, 2, 3, 4,$ and $5,$ yielding 4, 10, 20, 35, and 56 terms respectively. For the positron p-wave the function becomes

$$\sum_{j+m+n \leq N} \exp\left[-\frac{\alpha}{2}(r_1 + r_2)\right] r_{12}^j \left[C_{jmn} r_1^m r_2^n \vec{r}_1 + D_{jmn} r_1^n r_2^m \vec{r}_2 \right],$$

and $N = 1, 2, 3,$ and 4 yields 8, 20, 40, and 70 functions respectively. Twice as many as the e^-H case for a given N as a result of removing the symmetry requirement.

III. RESULTS AND DISCUSSIONS

The numerical work consisted mainly of doing the integrals in Eqs. (10) using the trial $\psi_{\pm}(\vec{r}_1, \vec{r}_2)$ described in section IIC, and solving Eqs. (12). Restricting the asymptotic form of ψ_{\pm} to the regular functions $j_m(kr)$ enabled us to do all the integrals exactly, in the sense that no cutoffs in the integrations over \vec{r}_1 and \vec{r}_2 were introduced. We now exhibit and discuss some typical calculations.

Figures 1 and 2 represent p-wave triplet and singlet "maps" for the lowest e⁻H energy studied, $k^2 = 0.01$, about 0.136 e.v. (The wave functions are normalized with an additional factor $1/\sqrt{k}$, so that λ discussed in part IIC becomes $\tan \eta/k^2$ rather than $\tan \eta/k$. This has no effect on the final answer; it was done simply because the p-wave phase $\eta_1 \sim k^2$ as $k \rightarrow 0$.)¹⁹ The parameter α defined in IIC is measured along the horizontal axis. These curves have a pleasantly smooth, parabolic behavior, with no apparent singularities. There may well be singularities that a finer partition of α would uncover, but the structure is clear enough for our purpose. If k were zero, we would expect strictly no singularities, because in that case we are guaranteed a minimum principle. For low energy, therefore, we're not surprised to find the singularities relatively scarce. (Each of the arrows in the figures point to the best value of $[\lambda]$ for corresponding N .) At this low energy the interaction is mainly due to polarization effects, since the incident particle is kept away from the atom by the centrifugal barrier.

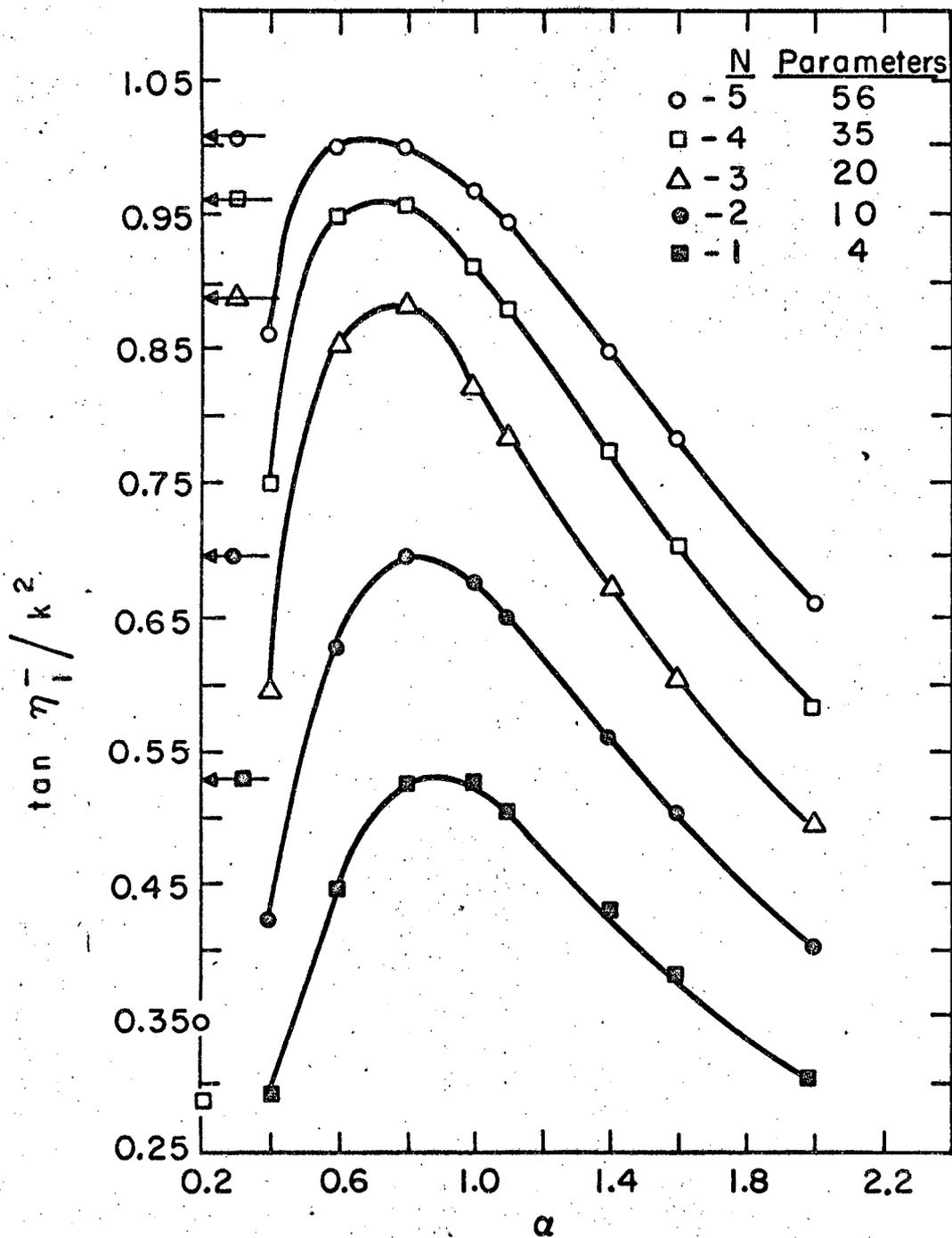


Fig. 1. λ vs. α , triplet p e^-H at $k = 0.1$ atomic unit. The arrows indicate the best $[\lambda]$ for each N .

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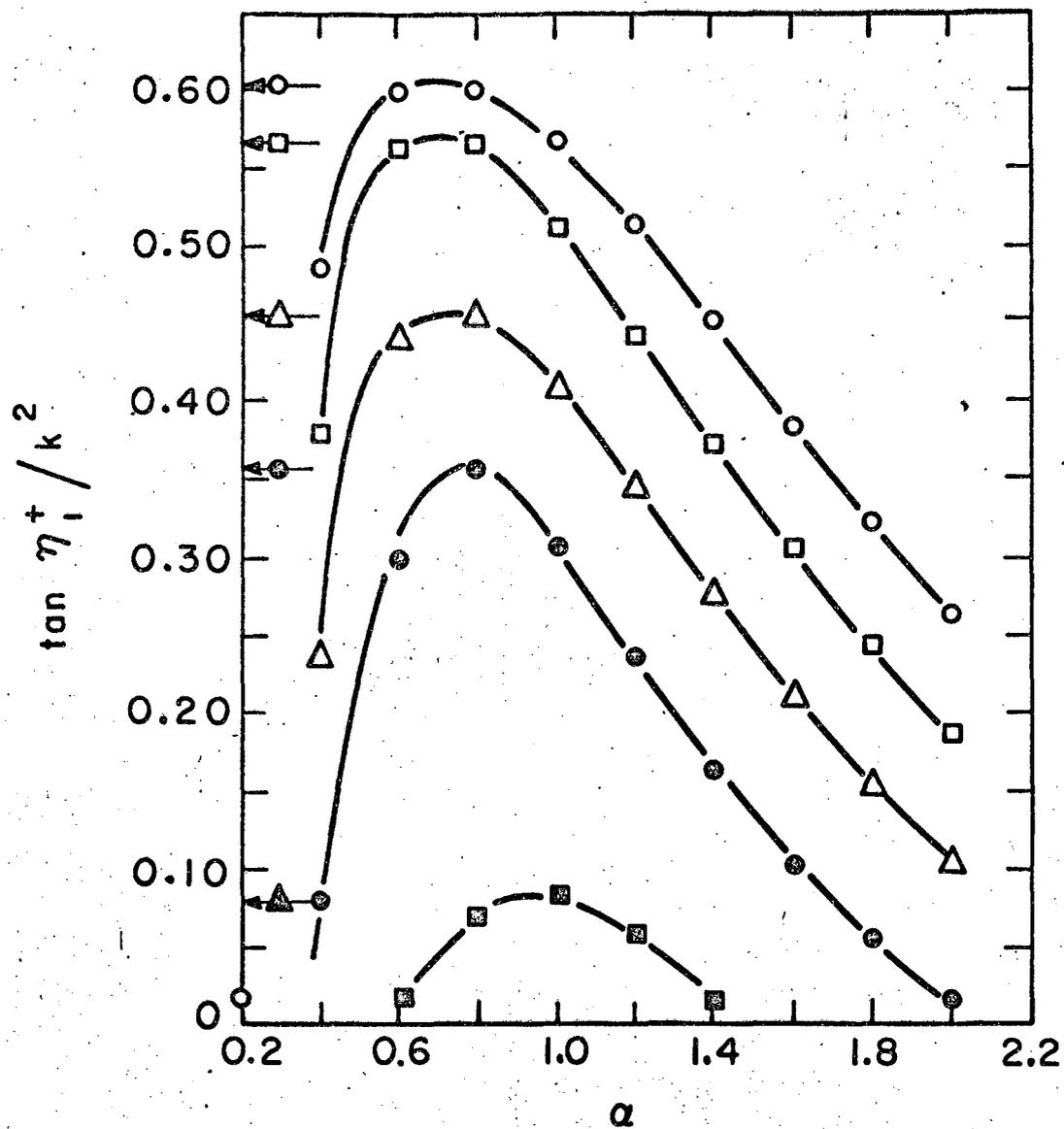
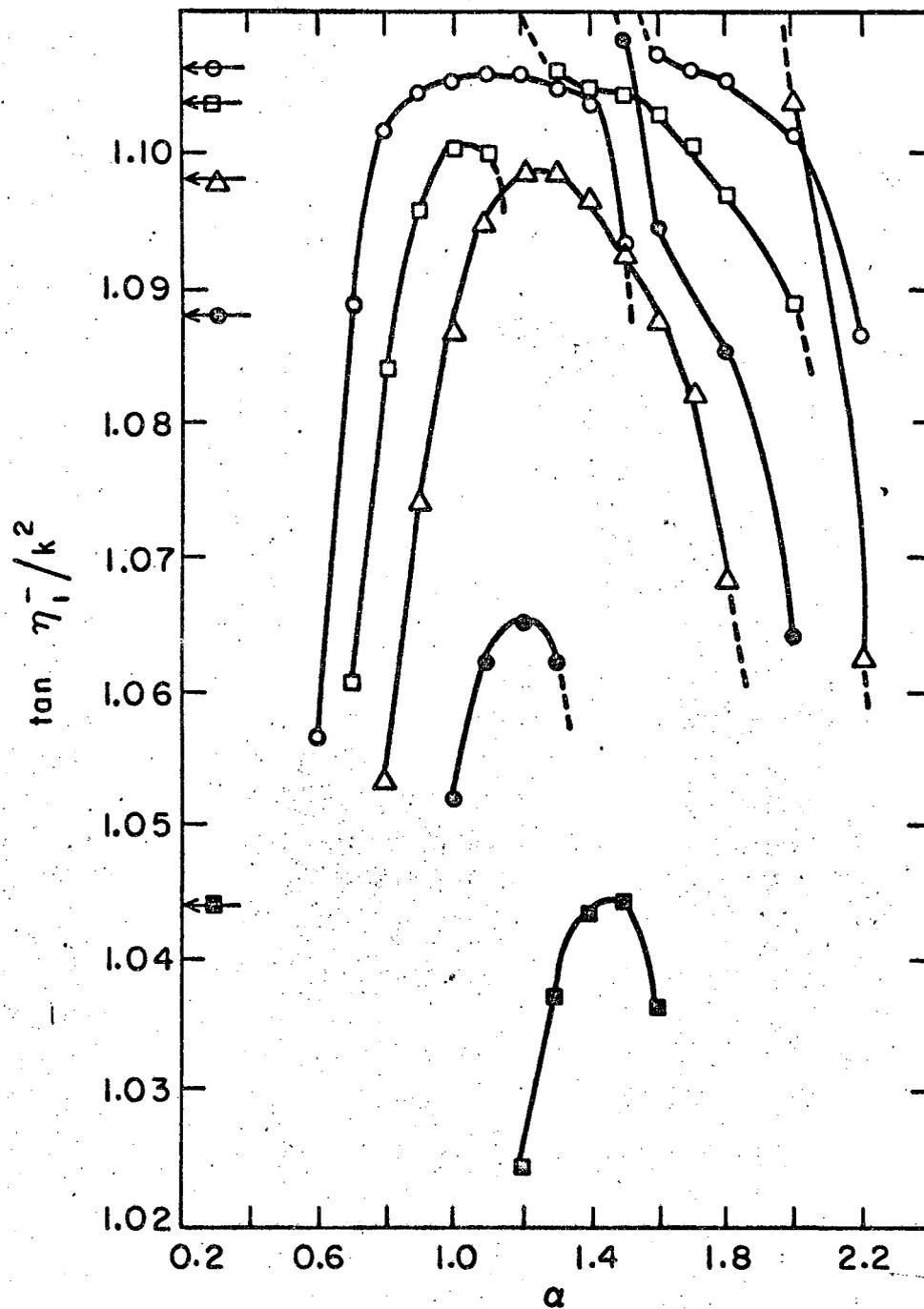


Fig. 2. λ vs. α , singlet p e⁻H at $k = 0.1$ atomic unit. Symbols are explained in Figure 1.

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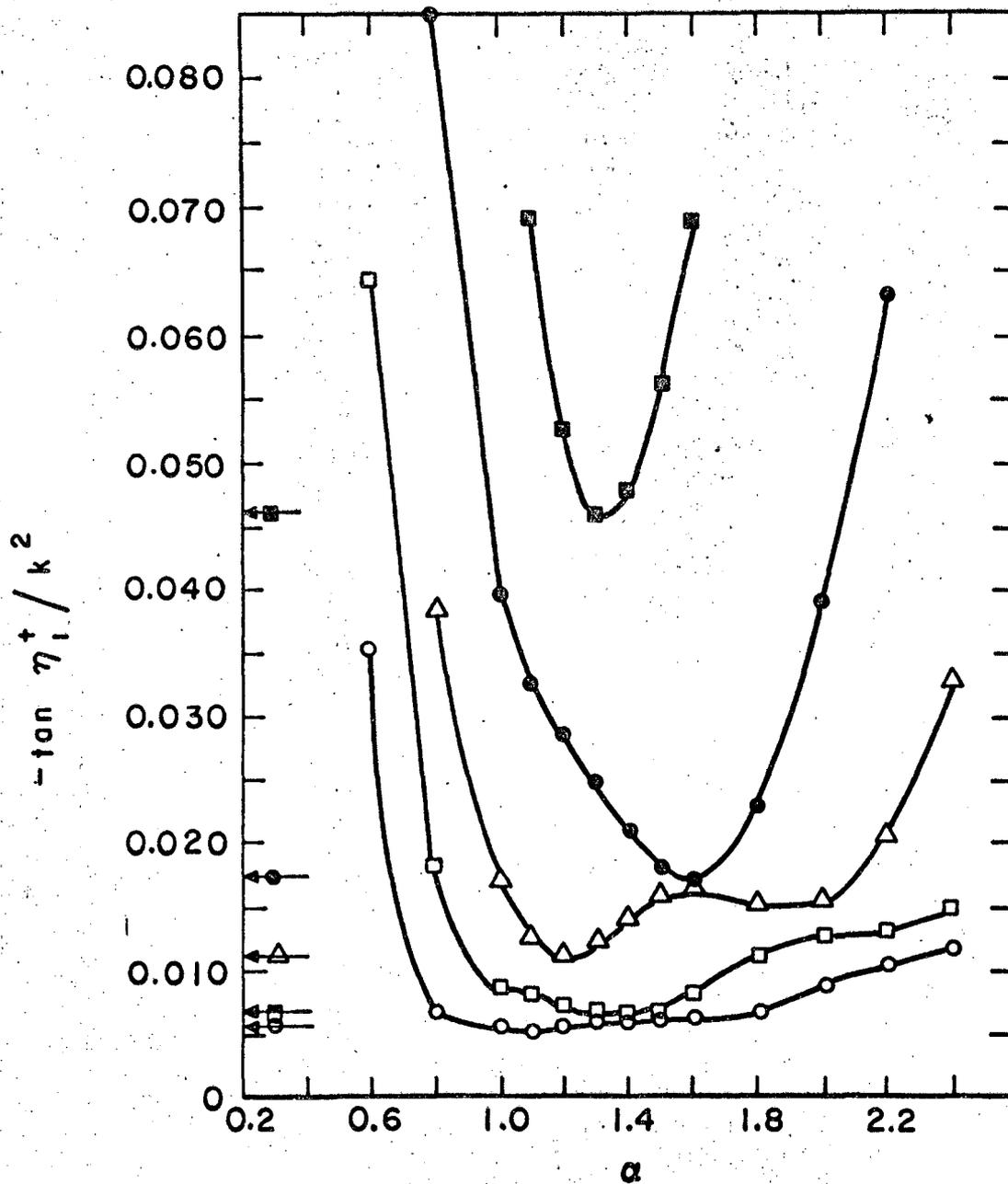
As k is increased, the character of the curves changes, as may be seen in Figs. 3 and 4 for $k = 0.5$. There is a marked flattening as N is increased, singularities appear (the dashed portions), and convergence (ignoring the singularities) is better than that at lower k . This improved convergence with increasing k may be understood by looking at the basis functions $u_1 = e^{-\alpha r} r^1$. They have a maximum at $r_0 = 1/\alpha$ and then rapidly tail off to zero as r increases. The dominant error term $\delta\psi$ in the wave function is something like $\sin(kr)/r^3$, as we saw in section IID, part 1. For small k this error term is a slowly oscillating function with decreasing amplitude as r increases, which the u_1 find hard to imitate. At larger k the oscillations are faster, and successive oscillations more nearly cancel to give an "average" function that vanishes more rapidly as $r \rightarrow \infty$. The u_1 , whose purpose is to remove the error, therefore have an easier task.

In Figure 5 at $k = 0.8$ we find an embarrassment of singularities, but as before the flat regions are not difficult to recognize. As the energy approaches the threshold for excitation to the first excited atomic state, convergence becomes worse for another reason, pointed out by Schwartz.¹⁷ For $k^2 > 3/4$, the asymptotic part of the wave function has a term $e^{ik'r}$, where $k' = \sqrt{k^2 - 3/4}$. For k^2 slightly less than $3/4$, k' is a small imaginary number $i\epsilon$, and the wave function should have a term which behaves as $e^{-\epsilon r}$. For small positive ϵ this is a long tail and not easily constructed with our short-range functions. For $k = 0.866$ the singlet p results thus



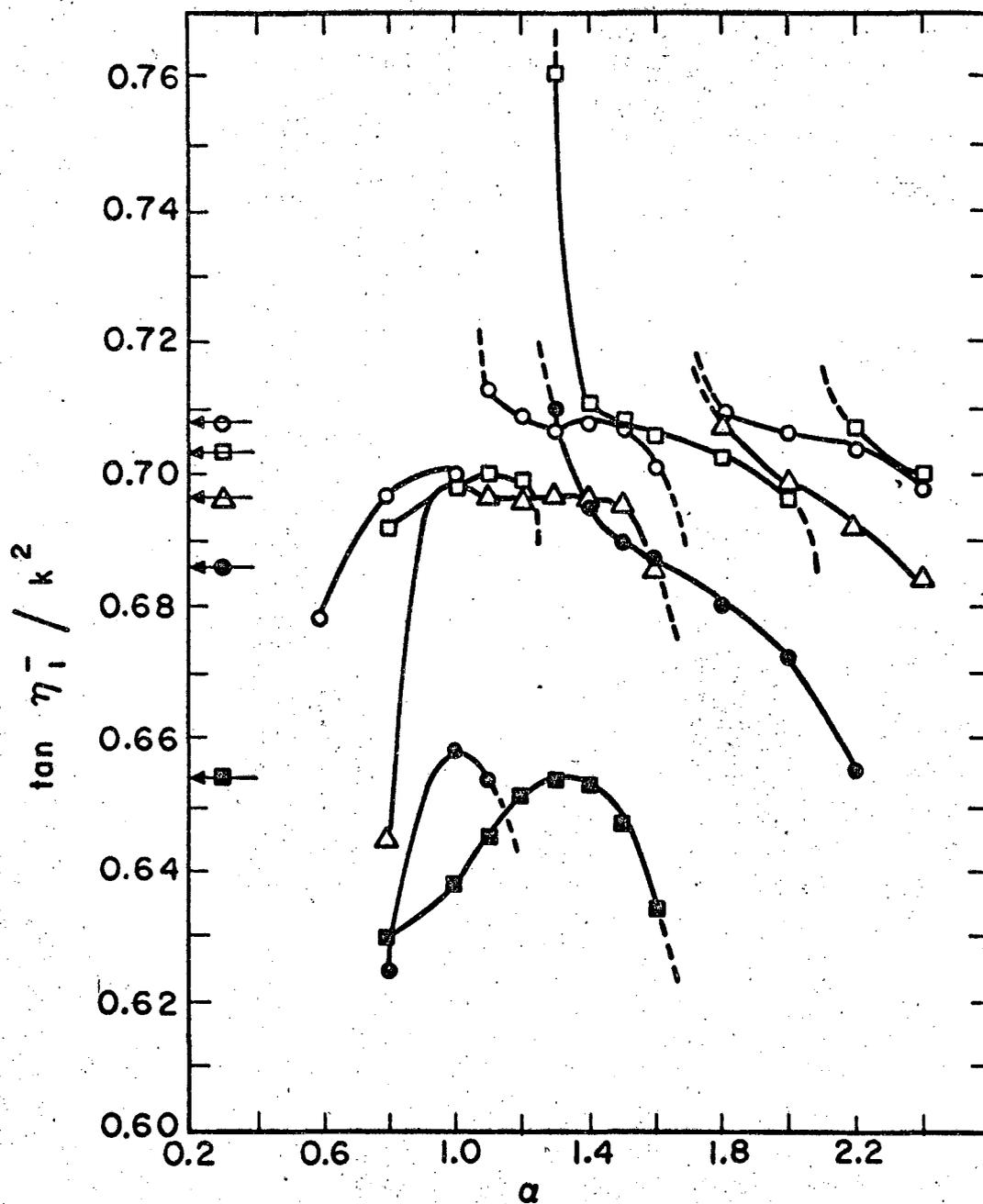
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Fig. 3. λ vs. α , triplet $p e^-H$ at $k = 0.5$ atomic unit. Symbols are explained in Figure 1.



MU-34737

Fig. 4. λ vs. α , singlet p e⁻H at $k = 0.5$ atomic unit. Symbols are explained in Figure 1.



MU-34738

Fig. 5. λ vs. α , triplet p e^-H at $k = 0.8$ atomic unit. Symbols are explained in Figure 1.

failed to converge as N was increased to 5. The triplet calculations were better behaved and hence more accurate in general, probably because of the (well-known) disposition of antisymmetry to account automatically for electron repulsion.

We were unable to find any resonance effects in the e^-H singlet or triplet p wave such as were reported by Burke and Schey²⁰ near threshold, only a moderate climb (about 0.04 radians) in the singlet phase. Some brief calculations at $k^2 = 0.68, 0.70, 0.72,$ and 0.74 also give smooth, monotonic behavior. Of course we may simply have failed to resolve a narrow resonance which is really there. (For example, the singlet s -wave e^-H resonance reported by Burke and Schey²⁰ takes place in the interval $k^2 = 0.70$ to 0.715 . This s -wave resonance is supported by some recent (unpublished) preliminary calculations of Schwartz, and we believe it is actually there.)

Exactly the same procedure was followed for positron-hydrogen scattering for s and p waves. The first inelastic channel appears at $k^2 = 0.5$ in this case, when it becomes possible to form positronium, so calculations extend only up to $k = 0.7$. The positron results are not as accurate as the electron results, because removing the symmetry requirement doubles the number of close-in functions for a given N (hence quadruples the size of the matrix M) and forces us to stop at a smaller maximum N . For the s wave, $N \leq 5$; while for the p wave $N \leq 4$. Otherwise the same remarks as for the e^-H apply to the behavior of $[\lambda]$ as a function of α .

The complete results are tabulated in Tables I and II. Row a refers to λ_t calculated using only the asymptotic wave function (no u_l 's), and row b to the corresponding $[\lambda]$. It is easily seen that row a is just the partial-wave Born approximation,⁴ and it was hoped that row b, a "variationally-improved Born approximation" might yield good results and save the (considerable) labor in solving Eqs. (12). The p-wave corrections--those large enough to detect--are all in the wrong direction, however. At least the failure is unequivocal.

O'Malley et al.¹⁹ have shown that when polarization effects are taken into account,

$$\tan \eta_l = \frac{2.25 \pi}{(2l+3)(2l+1)(2l-1)} k^2 + \dots$$

for $l \geq 1$, which agrees reasonably (within 20%) with our "full-treatment" η_l^\pm for small k . The Born approximation (both straight and variationally corrected) with no allowance for polarization effects is apparently quite inadequate, however, giving the dependence (from Table I) $\eta \sim k^{2l+1}$ as $k \rightarrow 0$.

The complete s-wave e^+H results are essentially identical to those of Schwartz,¹⁷ who used a different asymptotic function. We also did e^-H s-wave singlet and triplet calculations (not shown here) at $k = 0.1, 0.4,$ and 0.6 , and again reproduced Schwartz's results.

In all cases $[\lambda]$ increases monotonically with N . See, for example, Figs. 1 through 5. Therefore, while we cannot prove it, we

TABLE I. Electron-hydrogen phase shifts (in radians), singlet (η_ℓ^+) and triplet (η_ℓ^-) for total angular momentum $\ell = 1, 2, 3$. Row (a) is the Born approximation, (b) the variationally corrected Born approximation, (c) the probable lower bound, and (d) the most probable value. The number in parentheses is the probable error in the preceding digit.

k (atomic units)		η_1^-	η_1^+	η_2^-	η_2^+	η_3^-	η_3^+
0.1	(a)	0.0017	-0.0013	0.000004	-0.000003		
	(b)	0.0017	-0.0013	0.000004	-0.000003		
	(c)	0.0101	0.006				
	(d)	0.0114(6)	0.007(1)				
0.2	(a)	0.0130	-0.0092	0.00012	-0.00008		
	(b)	0.0130	-0.0092	0.00012	-0.00008		
	(c)	0.0448	0.0146				
	(d)	0.0450(1)	0.0147(2)				
0.3	(a)	0.0385	-0.0266	0.00079	-0.00052		
	(b)	0.0385	-0.0266	0.00079	-0.00052		
	(c)	0.1059	0.0163				
	(d)	0.1063(2)	0.0170(4)				
0.4	(a)	0.0771	-0.0510	0.0027	-0.0017	0.00010	-0.00006
	(b)	0.0769	-0.0512	0.0027	-0.0017	0.00010	-0.00006
	(c)	0.1866	0.0096				
	(d)	0.1872(3)	0.0100(2)				
0.5	(a)	0.1229	-0.0772	0.0067	-0.0040	0.00038	-0.00022
	(b)	0.1220	-0.0778	0.0067	-0.0040	0.00038	-0.00022
	(c)	0.2695	-0.0014				
	(d)	0.2699(2)	-0.0007(5)				
0.6	(a)	0.1694	-0.0994	0.0129	-0.0071	0.0010	-0.00055
	(b)	0.1667	-0.1008	0.0129	-0.0071	0.0010	-0.00055
	(c)	0.3405	-0.010				
	(d)	0.3412(3)	-0.009(1)				

TABLE I (Cont.)

k (atomic units)	η_1^-	η_1^+	η_2^-	η_2^+	η_3^-	η_3^+	
0.7	(a)	0.2112	-0.1137	0.0211	-0.0107	0.0022	-0.0011
	(b)	0.2058	-0.1164	0.0211	-0.0107	0.0022	-0.0011
	(c)	0.3918	-0.014				
	(d)	0.3927(5)	-0.013(2)				
0.8	(a)	0.2447	-0.1190	0.0308	-0.0141	0.0039	-0.0017
	(b)	0.2367	-0.1227	0.0307	-0.0141	0.0039	-0.0017
	(c)	0.425	-0.006				
	(d)	0.427(5)	-0.01(1)				
0.860	(c)		+0.019				
	(d)		+0.03(1)				
0.866	(a)	0.2630	-0.1172				
	(b)	0.2524	-0.1218				
	(c)	0.44	+0.054				
	(d)	0.44(2)					

TABLE II. Positron-hydrogen phase shifts for $t = 0, 1, 2, 3$. The rows have the same significance as in Table I.

k (atomic units)	η_0	η_1	η_2	η_3
0.1 (a)	-0.099	-0.00025	-0.65×10^{-6}	-0.17×10^{-8}
(b)	-0.099	-0.00025	-0.65×10^{-6}	-0.17×10^{-8}
(c)	0.142	0.008		
(d)	0.149(2)	0.009(1)		
0.2 (a)	-0.192	-0.0019	-0.19×10^{-4}	-0.21×10^{-6}
(b)	-0.192	-0.0019	-0.19×10^{-4}	-0.21×10^{-6}
(c)	0.186	0.032		
(d)	0.189(1)	0.033(1)		
0.3 (a)	-0.274	-0.0060	-0.00014	-0.32×10^{-5}
(b)	-0.275	-0.0060	-0.00014	-0.32×10^{-5}
(c)	0.165	0.064		
(d)	0.168(2)	0.065(1)		
0.4 (a)	-0.343	-0.013	-0.00052	-0.20×10^{-4}
(b)	-0.346	-0.013	-0.00052	-0.20×10^{-4}
(c)	0.118	0.099		
(d)	0.121(2)	0.102(1)		
0.5 (a)	-0.399	-0.023	-0.0014	-0.81×10^{-4}
(b)	-0.405	-0.023	-0.0014	-0.81×10^{-4}
(c)	0.061	0.130		
(d)	0.062(1)	0.132(1)		

TABLE II (Cont.)

k (atomic units)	η_0	η_1	η_2	η_3
0.6 (a)	-0.444	-0.036	-0.0029	-0.00023
(b)	-0.453	-0.036	-0.0029	-0.00023
(c)	0.002	0.153		
(d)	0.007(2)	0.156(2)		
0.7 (a)	-0.477	-0.050	-0.0052	-0.00055
(b)	-0.492	-0.050	-0.0052	-0.00055
(c)	-0.053	0.175		
(d)	-0.051(2)	0.178(3)		

believe that $[\lambda]$ calculated for the largest N (5 in the e^{-H} case) is a lower bound on the correct λ and hence gives a lower bound on the phase η . Accordingly, this number appears in row c. Row d is the most probable value for the phase, obtained by extrapolating to $N = \infty$. A crude analysis of successive maxima shows that where convergence occurs, it is faster than $1/N^2$, but probably not as fast as x^N . Each sequence of stationary values is therefore extrapolated in three ways: assuming geometric convergence, assuming $1/N^4$, and assuming $1/N^2$. In general the average is taken as the most probable λ , and the average deviation as the probable error. The number in parentheses represents the probable error in the preceding digit.

It has been suggested that the difference between $[\lambda]$ and λ_t might be a reliable measure of the accuracy of a variational calculation. It is usually true that $|\lambda - \lambda_t|$ is smallest in the regions (of α) where the curves are stationary; however, as in earlier calculations,¹⁴ this quantity actually passes through zero occasionally and could easily lead to an overestimate of the accuracy. In Tables I and II, for example, the ordinary and the variationally improved Born approximations are in all cases very close, yet quite wrong.

In the p-wave calculations the value of α at which a stationary value of $[\lambda]$ occurs for given N increases (with some exceptions) with increasing k , as may be seen from Figs. 1 through 5.

This is probably because higher energies allow the incident particle to approach the atom more closely, thus pulling in the wave function. The value of α that permits an optimum reproduction of the true wave function then increases as k is increased, since this decreases the value of r for which $e^{-\alpha r} r^m$ has its maximum. Near zero energies this behavior is quite pronounced, becoming less so as k exceeds approximately 0.4 (2.2 e.v.). In the positron s-wave calculation, the effect was not observed, which is quite reasonable since there is no centrifugal barrier in that case.

In some instances the variational coefficients C_1 were monitored during the calculation to see if they converged. That is, to see if as N was increased, a particular C_1 might approach or stabilize at some constant value. If the u_1 had been chosen orthogonal with the operator $H - E$ then each C_1 , once determined, would never change, since the matrix M would be diagonal. The u_1 were not so chosen, there is no apparent reason to expect such convergent behavior, and it did not occur.

The e^-H p-wave phase is compared with some other theoretical calculations in Fig. 6. In Fig. 7 we plot the theoretical e^-H cross section calculated from Schwartz's¹⁷ s-wave and our p-wave results according to

$$Q_T = \sum_{l=0}^{\infty} Q_l, \quad \text{where}$$
$$Q_l = \frac{(2l+1)\pi}{k^2} \left[3 \sin^2 \eta_l^- + \sin^2 \eta_l^+ \right]$$

for unpolarized beams.

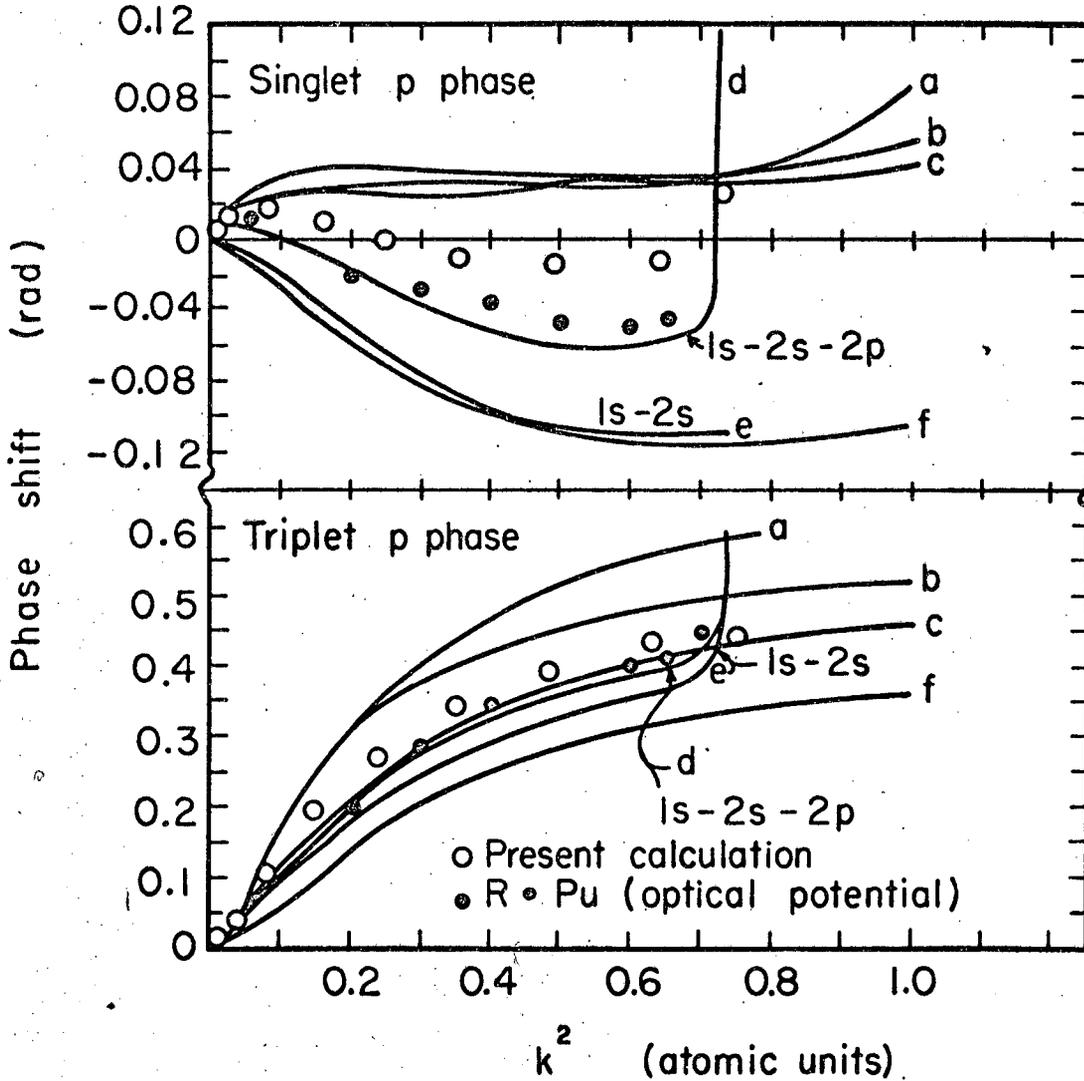
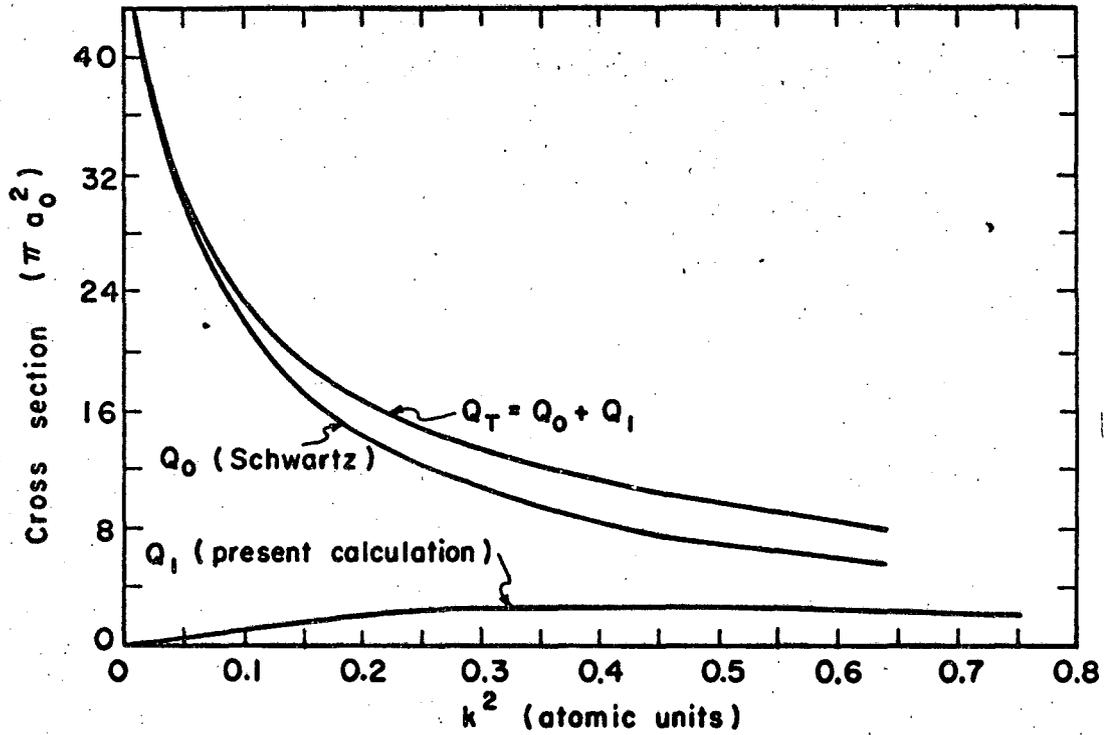


Fig. 6. Our phase shifts alongside theoretical calculations of Bransdon,²¹ et al. (a), Malik and Trefftz²³ (b), Temkin and Lamkin²² (c), Burke and Schey²⁶ (d), Smith et al.²⁴ (e), John²⁵ (f), and Pu.²⁷ Each curve represents a different approximation. The eigenfunction-expansion calculations are labeled by the states that are retained in the expansion (see the introduction); e.g., John retained only the 1s state of atomic hydrogen in his calculation.

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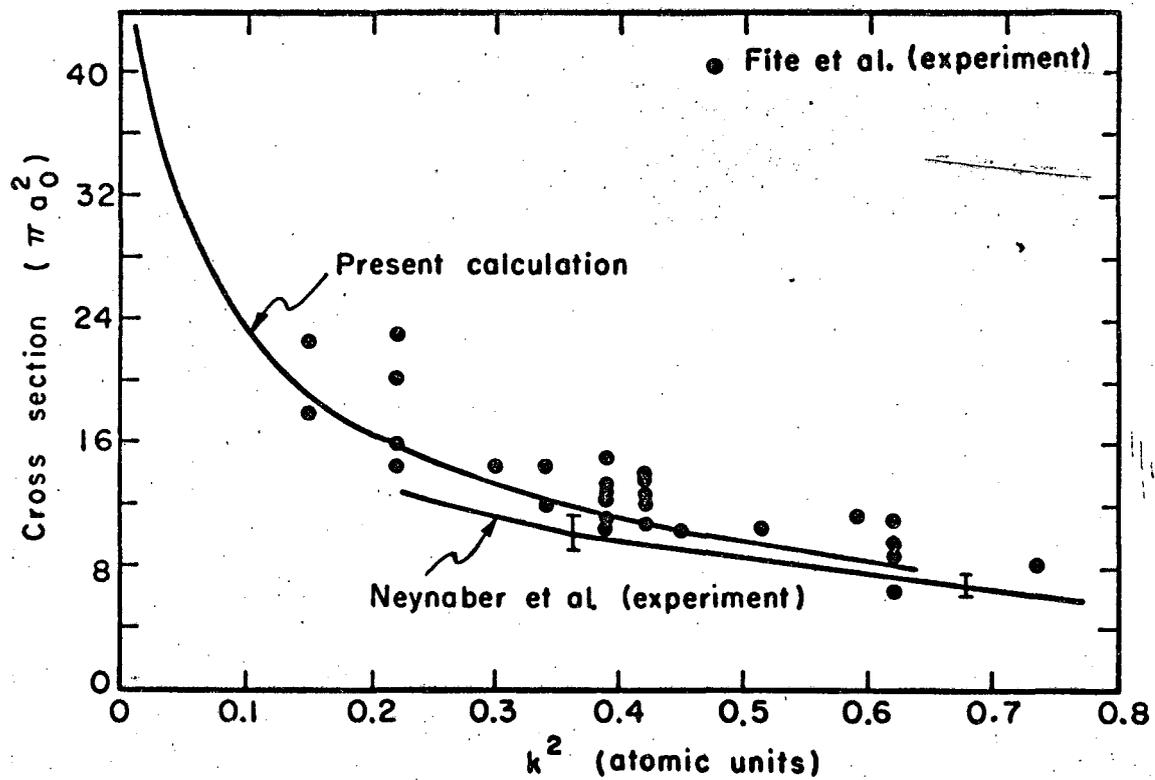


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Fig. 7. Electron-hydrogen cross sections computed from $\ell = 0, 1$ phase shifts. Cross sections are in units πa_0^2 (a_0 the Bohr radius), and k^2 is in atomic units.

In Figure 8 the experimental results of Fite et al.²⁷ and Neynaber et al.²⁸ are shown with our Q_T . Our results are in agreement with the experimental data, but there is such a large scatter in the data that it is impossible to confirm the theoretical calculations on that basis alone. Other calculations yielding significantly different phase shifts from our own also fall inside the experimental limits.

These calculations were performed on an IBM 7094 computer, using single precision (8 decimal figure) arithmetic. The number of variational parameters used was limited by the solution of Eqs. (12). For a maximum of 56 parameters (corresponding to $N \leq 5$), our code takes 0.10 minute of computer time for a given k and α . About a dozen points (a dozen α) are usually needed to resolve the structure at a given energy, so a complete calculation at one energy takes approximately 1.2 minutes. Taking $N \leq 6$ means 84 parameters and increases the total time to approximately $(84/56)^3 \times 1.2 = 4.0$ minutes. This is still within reason and was tried, but it was found that numerical roundoff errors in solving (12) then grew so large that the answers were unreliable. So we stopped at $N \leq 5$ for e^-H p wave, and $N \leq 4$ for e^+H .



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Fig. 8. Comparison of theoretical and experimental total cross sections for elastic electron-hydrogen scattering.

IV. CONCLUSIONS

In carrying out the complete variational calculation, we find that the singularities are somewhat annoying, but easily tolerable since we know their origin and can ignore them. We believe that the variational principle for elastic electron-hydrogen scattering provides the most accurate partial-wave phase shifts of any method available, when applied as above with a sufficiently rich set of functions u_i . While it may not be practical for direct application to more complicated systems (e.g. many-electron atoms), it should serve as a useful standard against which other approximations may be judged.

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